CHEMICAL REAGENTS

Dr C. KRAUCH

SECOND REVISED EDITION

Published at → 7.00
Mail out 6 pm 4.50
JOHN M. ANDREAS

© Raymond Pettibon

RESEARCH LIBRARY
THE GETTY RESEARCH INSTITUTE

JOHN MOORE ANDREAS COLOR CHEMISTRY LIBRARY FOUNDATION

JOHN M. ANDREAS

CHEMICAL REAGENTS

CHEMICAL REAGENTS

THEIR USES, METHODS OF TESTING FOR PURITY AND COMMERCIAL VARIETIES

BY

DR. C. KRAUCH

CHEMIST TO THE FIRM OF E. MERCK, DARMSTADT

TRANSLATED FROM THE THIRD GERMAN EDITION

SECOND ENGLISH EDITION, REVISED AND ENLARGED

BY

H. B. STOCKS, F.I.C., F.C.S.

LONDON

SCOTT, GREENWOOD & SON

"THE OIL AND COLOUR TRADES JOURNAL" OFFICES

8 BROADWAY, LUDGATE, E.C. 4

1919

[*The sole right of translation into English rests with Scott, Greenwood & Son*]

First English Edition 1902
Second English Edition, Revised and Enlarged . July 1919

ABERDEEN: THE UNIVERSITY PRESS

THE GETTY RESEARCH
INSTITUTE LIBRARY

PREFACE.

The purity of the reagents employed in analytical and research work being of the utmost importance, it is essential that speedy and reliable tests for the detection of impurities which may occur in any particular commodity should be available. This information is to be found in a very comprehensive form in Dr. Krauch's work on "The Testing of Chemical Reagents for Purity".

This work was originally translated into English by J. A. Williamson, F.C.S., and L. W. Dupré from the third German edition, and was issued in October, 1902. The present work is based on the original, but has been revised, enlarged, and brought up-to-date, so that a considerable amount of new material is now available.

As pointed out by the translators, references have been made in most cases to English abstracts from original communications, and instead of referring to the numerous German text-books on chemical analysis mentioned by the author, the corresponding English works are quoted. The translators also acknowledge the valuable help given by the author in supplying additions and corrections, the result of his experience since the third German edition was published.

The Latin titles of the reagents are those of the Pharmacopœia Germanica; these have been retained since they may be of service for the recognition of certain chemicals in foreign lists.

In conducting the various tests, the author emphasises rigid adherence to the degree of concentration, the amount of reagent employed, and the method in which the test is to be carried out.

In this edition all the new reagents, such as dimethylglyoxime, nitron, benzidine, etc., have been introduced and their uses described; much new matter has also been added in connection with the older reagents. Temperatures are given in all cases in degrees centigrade, while the whole of the molecular weights have been re-calculated from the International Atomic Weights for 1918.

LONDON, *June*, 1919.

INTRODUCTION.

ON REAGENTS AND REACTIONS IN GENERAL.—*Chemical Reagents* include all preparations used for the various chemical and microscopical investigations for the identification of the elements and their compounds, and also for distinguishing animal and vegetable tissues. They are also employed for determining the chemical constitution and reactions of numerous substances.

According to the chemical significance of the word "reaction," all substances which produce chemical change ought, strictly speaking, to be classed under the heading of "Chemical Reagents". The term, however, is chiefly used in a limited sense to designate a means for identification. The word is not usually applied to substances employed for chemical decompositions on the manufacturing scale. The reagents are divided into several groups according to their use and method of reaction. Some are employed in the wet and some in the dry state, the latter constituting those used under circumstances where the liquid state necessary for chemical action can only be attained by means of fusion; the former are used in solution. Some dry reagents are also used to promote or facilitate a state of fusion, and many are employed in blowpipe analysis. The other class includes the various acids, halogens, metals, bases, salts, dyes, and indifferent vegetable compounds; also the ordinary solvents.

In addition to reagents used for qualitative and quantitative analysis, special mention must be made of those for volumetric analysis and ultimate organic analysis, and also those employed for the detection of alkaloids, etc., in forensic analysis. The reagents used in microscopical investigations form another class. Owing to the fact that the same reagents are employed in more than one of these classes, it has been considered advisable to avoid confusion by arranging them alphabetically.

The term "Chemical Reaction" is meant to imply the chemical decomposition undergone by a substance whereby new molecules are formed with the production of an entirely new compound and properties. As these chemical decompositions owe their origin to some more or less violent action produced by heat, light, electricity, or the interaction of two chemical compounds, the term "reaction" is a very appropriate one.

In analytical investigations, the power of distinguishing between the various reactions depends upon the properties of the products of decomposition, and the manner in which they appeal to the sense of colour, smell, sound, etc. It is often necessary to closely observe certain precautions in order to bring about a successful reaction, and the author frequently calls attention to these precautions in notes, and also gives the degree of concentration necessary for a particular reaction. That reactions under certain conditions fail to take place is explained by the fact that chemical decomposition and formation are controlled by the powers of affinity of the elements present, and, in turn, these depend upon the external influences of heat, light, and degree of concentration under which the two reacting substances meet. To this may be added that, unless the proper degree of concentration be strictly observed, traces of substances supposed to be present may not appear, owing to the solubility of the precipitate in the solution. It is, therefore, essential to pay most particular attention to the time, temperature, and proportions given for the various tests.

ACETIC ACID.—Acid. acetic. conc. puriss. ($C_2H_4O_2$). Mol. wt., 60·03. Clear, colourless liquid, with a sour pungent smell, solidifying about 10° C. Sp. gr., 1·064, containing about 96 per cent. acetic acid. B.p., 118°. Mixes with water in all proportions.

Note.—A weaker acid (about 90 per cent.) shows a sp. gr. of 1·071.

Tests for Impurities.—*Residue.*—On volatilisation of 10 gms. of the acid, no weighable residue must remain.

Note.—When larger quantities of the pure strong acid are volatilised, traces of a partially combustible organic residue remain; this should not, however, amount to more than one milligram in 50 c.c.

[1] *Heavy Metals and Earths.*—On diluting 10 gms. to 100 c.c., adding excess of ammonia, and subsequently ammonium sulphide and ammonium oxalate, no change should take place even after standing for some time, and slightly warming. On diluting 20 gms. to 100 c.c. and adding freshly prepared H_2S water, no brown colour should appear.

Sulphuric Acid.—10 gms. in 100 c.c. of water are heated to boiling, and barium chloride added; after standing for several hours no precipitate should have formed.

Hydrochloric Acid.—On treating 5 gms. in 50 c.c. of water with nitric acid and silver nitrate, no cloudiness should appear.

Empyreumatic Substances.—On adding 50 c.c. $\frac{n}{100}$ permanganate solution to 5 gms. of the acid diluted with 15 c.c. water, the pink colour should remain after standing 15 minutes.

Quantitative Estimation.—A weighed quantity is diluted with water, phenolphthalein added, and the acid titrated with

[1] In this and other parts of the work, the author has used for the sake of brevity the term "heavy metals". The metals indicated are at once recognised from the description of the test (e.g. addition of ammonium sulphide), thus saving elaborate detail.

normal alkali (free from carbonate). 1 c.c. normal alkali = ·06003 gm. $C_2H_4O_2$. The purity of the acid may be gauged from the temperature at which it assumes the glacial state, the stronger the acid the higher the temperature at which it solidifies. Thus an acid containing 0·5 per cent. of water becomes glacial at 15·65°, with 2·91 per cent. at 11·95°, and with 6·54 per cent. at 7·1°. When the acid contains 49·4 per cent. of water, the solidifying point is reduced to − 19·8°. The specific gravity of the pure acid affords an easy means of ascertaining its strength.

SPECIFIC GRAVITY OF ACETIC ACID AT 15° (OUDEMAN'S).

Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.
0·9992	0	1·0363	26	1·0631	52	1·0748	78
1·0007	1	1·0375	27	1·0638	53	1·0748	79
1·0022	2	1·0388	28	1·0646	54	1·0748	80
1·0037	3	1·0400	29	1·0653	55	1·0747	81
1·0052	4	1·0412	30	1·0660	56	1·0746	82
1·0067	5	1·0424	31	1·0666	57	1·0744	83
1·0083	6	1·0436	32	1·0673	58	1·0742	84
1·0098	7	1·0447	33	1·0679	59	1·0739	85
1·0113	8	1·0459	34	1·0685	60	1·0736	86
1·0127	9	1·0470	35	1·0691	61	1·0731	87
1·0142	10	1·0481	36	1·0697	62	1·0726	88
1·0157	11	1·0492	37	1·0702	63	1·0720	89
1·0171	12	1·0502	38	1·0707	64	1·0713	90
1·0185	13	1·0513	39	1·0712	65	1·0705	91
1·0200	14	1·0523	40	1·0717	66	1·0696	92
1·0214	15	1·0533	41	1·0721	67	1·0686	93
1·0228	16	1·0543	42	1·0725	68	1·0674	94
1·0242	17	1·0552	43	1·0729	69	1·0660	95
1·0256	18	1·0562	44	1·0733	70	1·0644	96
1·0270	19	1·0571	45	1·0737	71	1·0625	97
1·0284	20	1·0580	46	1·0740	72	1·0604	98
1·0298	21	1·0589	47	1·0742	73	1·0580	99
1·0311	22	1·0598	48	1·0744	74	1·0553	100
1·0324	23	1·0607	49	1·0746	75		
1·0337	24	1·0615	50	1·0747	76		
1·0350	25	1·0623	51	1·0748	77		

Note.—The specific gravities above 1·0553 in each case represent two liquids of very different strength. In order to ascertain whether the strength of the acid exceeds that with the maximum density (78 per cent.) or the reverse it suffices to add a little water; in the case of a stronger acid the specific gravity increases, but it decreases if the acid is weaker.

Uses and Storage.—For analytical purposes, acetic acid is chiefly used as a solvent and neutralising agent. For use as a reagent the puriss. concentrated acid is usually diluted with three times its weight of water. For some purposes, however, the strong acid is used—e.g. Goldenberg's method for the estimation of tartaric acid ("J.S.C.I.," 1888, p. 349) and Adamkiewicz's test for albumen ("J.C.S.," 1875, pp. 172, 919). It is advisable to use a glacial acetic acid of known strength in making up the dilute acid (1½ per cent., or even less) employed in microscopy. The acid must be kept in well-stoppered glass bottles, and since the glacial acid solidifies in the winter time if kept in a cold room, in order to avoid accident it is necessary to thaw it very carefully, particularly if stored in large bottles.

Commercial Varieties.—In addition to the above acid, generally used for analytical work, the following kinds of acetic acid are placed on the market: (1) Glacial acetic acid, a very concentrated acid (about 99 per cent.), dissolving oil of lemons in all proportions, and standing all the tests for purity, with the exception of that for empyreumatic substances; it is stronger than the puriss. (2) Glacial acetic acid, a less concentrated acid, dissolving oil of cloves.

Note.—The solubility of certain essential oils in acetic acid presents a rough method of determining the strength. Oil of lemons dissolves only in an acid containing not more than 2 per cent. of water; oil of cloves will dissolve in acids containing up to 10 per cent.

Acid acetic, pure (1·06), acid acetic, puriss. (1·06), contain 50 per cent. acid acetic, dilut., pure (1·04), and acid acetic, dilut., puriss. (1·04), 40 per cent. of the strong acid; those marked puriss. pass all the tests prescribed, but the pure acids generally contain traces of empyreumatic substances.

Acidum aceticum of the British Pharmacopœia contains 33 per cent. of acetic acid and Acidum aceticum dilutum, 4·27 per cent.

ACETIC ANHYDRIDE.—Acid. acetic. anhydric. $((C_2H_3O)_2O)$. Mol. wt., 102·05. Colourless liquid, boiling at 138°, having an odour of acetic acid. Sp. gr., 1·0799 at 15·2°.

When acetic anhydride is poured into water it at first sinks to the bottom of the vessel, but slowly combines with the water to form acetic acid. It must be carefully preserved in well-stoppered vessels. The solution (1 : 50) must give no reaction on adding nitric acid and silver nitrate, and its strength is estimated volumetrically with normal alkali. 1 c.c. normal alkali = 0·05102 gm. acetic anhydride. It is not often used in analysis, but is employed, *inter alia*, in the estimation of lanoline (B. Fischer, "Die neueren Arzneimittel," 1889, p. 79), in the acetine method for the estimation of glycerine (Sutton, "Vol. Anal.," 7th ed., p. 365), in the Liebermann-Storch test for rosin (Lewkowitsch, "Oils, Fats, and Waxes," vol. i., p. 610, 5th ed.), also in the tests for chtolesterol and phytosterol (*ibid.*, p. 588).

Hirschsohn, in determining the essential oils of the coniferæ, employed a so-called acetic acid reagent consisting of 10 gms. acetic anhydride and 5 drops pure concentrated sulphuric acid ("Pharm. Ztg.," 1891, p. 725).

ACETONE. — Acetonum puriss. Dimethylketone $CH_3 . CO . CH_3$. Mol. wt., 58·05. A clear, colourless, mobile liquid, having a smell resembling ether. Sp. gr., 0·797-0·798. B.p., 56°-57°. Dissolves in water but separates on addition of soluble salts.

Tests for Impurities.—*Volatile Matter.*—30 gms. must leave no residue on evaporation.

Aldehyde.—No reaction should be produced with Schiff's reagent or with ammoniacal silver nitrate.

Solubility and General Appearance.—Pure acetone is perfectly clear and colourless, and miscible with water in all proportions, without showing any turbidity.

Action of Permanganate.—On the addition of 1 drop of potassium permanganate solution (1 : 1000) to 10 c.c. of the acetone, the pink colour must not be completely discharged at the end of 15 minutes. This test serves to detect the presence of aldehyde. An acetone which contains 0·5 per cent. by volume of aldehyde discharges the colour in 5 minutes, and 0·25 in 10 minutes. Free mineral acid must not be present.

Water.—Schweitzer and Lungwitz ("Chem.-Ztg.," 1895, p. 1384; "J.S.C.I.," 1895, p. 1069) detect the presence of water

in acetone by adding to 50 c.c. of the sample 50 c.c. of petroleum spirit (b.p. 40°-60°). In the event of water being present, two layers are formed, which does not occur when pure acetone is similarly treated. It is a remarkable fact that if 2 c.c. of water be added to 50 c.c. of chemically pure acetone, on applying this test, instead of the lower layer occupying a volume of 2 c.c. it is observed to measure 5-7 c.c. Pure acetone must, therefore, show no alteration on shaking with petroleum spirit.

Boiling Point (see above).—Concerning the estimation of the b.p. and sp. gr. of acetone, see Geehmugden ("Zeit. f. anal. Chem.," 1896, pp. 503, 504; also "J.C.S.," 1896, pt. 2, p. 679).

Note.—It is a well-known fact that in boiling-point determinations varying results are obtained depending on the material and nature of the vessels employed for that purpose. To obtain concordant results the author always uses a small copper still, as suggested by Bannow in his Report on the Commission on Analytical Methods for Fractional Distillation, published in the "Chemische Industrie," 1886, p. 328.

Acidity.—Acetone must not redden blue litmus paper.

Acetone heated with rhamnose and HCl yields a transient rose colour followed by a yellowish-green fluorescence (R. Tritsch, "F. Anal. Chem.," 1910, 49, 94-97; "J.S.C.I.," 1910, p. 456).

Quantitative Estimation.—Krämer's iodoform method may be employed (conversion into iodoform by means of excess of iodine solution, in presence of a solution of sodium carbonate). On the quantitative estimation of acetone, see also under "Methyl Alcohol". A new method of estimation of acetone with phenylhydrazine has been proposed by Strache, which is said to be better than the iodoform method ("Zeit. f. anal. Chem.," 1892, p. 573 *et seq.*, and "J.S.C.I.," 1893, p. 185).

Note.—The above tests are mentioned in part by Guttmann (Dingler's "Polytechn. Journal," 1894, pp. 96-111) as being chiefly used when a specially pure acetone is demanded, e.g. in the manufacture of smokeless powders. Concerning this test, see Klar, ("J.S.C.I.," 1897, p. 722 *et seq.*).

Uses and Storage.—Acetone is largely used as a solvent for fats, oils, etc., in chemical investigations. It should be kept in well-stoppered bottles in a cool place, as it is easily volatile and inflammable.

Commercial Varieties.—In addition to pure acetone, the quality used for technical purposes (manufacture of smokeless powders) can also be obtained in a very pure state in the market. Guttmann (loc. cit.) found it to have a sp. gr. of 0·7965, and 98 per cent. distilled over between 56·2° and 56·4°. Good commercial qualities gave no reaction with permanganate test in several minutes, and he found the acidity of those samples which were perfectly soluble to be not higher than 0·00225 per cent. (See Klar, loc. cit.)

ALCOHOL, AMYL.—Alcohol amylic. pur. Amyl alcohol. Isobutyl carbinol ($C_5H_{12}O$). Mol. wt., 88·10. B.p., 131°-132°. Sp. gr., 0·814. Clear, colourless liquid, without action on litmus paper. Soluble in water 1 in 39, mixes with alcohol and ether in all proportions.

Note.—Crude amyl alcohol, or fusel oil, is easily distinguished from the pure by the difference in specific gravity and boiling point.

Tests for Impurities.—*Volatile Matter.*—On evaporating 10 gms. on the water bath no residue must remain.

Furfurol.—5 c.c. amyl alcohol, mixed with 5 c.c. concentrated sulphuric acid, must show only a slight yellow or reddish colour.

Water and Ethyl Alcohol.—Mixed with an equal volume of petroleum ether should not become turbid.

Boiling Point, etc.—See above.

Note.—The ordinary commercial samples of amyl alcohol are coloured brown to blackish-brown by sulphuric acid. Amylic alcohol, which gives a colourless liquid on mixing with sulphuric acid, can only be obtained according to L. v. Udranzky (see that author on the furfurol reaction, "J.S.C.I.," 1889, p. 309) by repeated and troublesome treatment of the commercial preparation with concentrated sulphuric acid, etc. Perfectly pure amyl alcohol can only be obtained by the decomposition of pure potassium amyl sulphate. For most analytical purposes, a carefully-rectified preparation, with the correct boiling point and specific gravity, and conforming with the above tests, is sufficiently good, but there are certain processes in which it is necessary to have a preparation giving no trace of the furfurol reaction.

Quantitative Estimation. — Estimation of the boiling point is sufficient to determine its strength.

Amyl alcohol may be detected by heating with glacial

acetic acid and concentrated sulphuric acid, amyl acetate being evolved.

Uses.—Amyl alcohol is used in forensic analysis for the extraction of alkaloids, and is also employed in the analysis of foods and drugs. See also H. Droop Richmond's "Dairy Chemistry" regarding its use in milk testing.

Commercial Varieties.—Fusel oils of different degrees of purity are found on the market. Ordinary commercial fusel oils often contain only 30 per cent. of pure amyl alcohol. The "Chemiker. Zeitung," 1889, p. 1062, reports a commercial sample containing pyridine. (See also "J.S.C.I.," 1889, p. 734.)

ALCOHOL, ETHYL.—Alcohol absolut. pur. (C_2H_6O). Mol. wt., 46·05. Clear, colourless liquid. The sp. gr. at 15·5° is 0·796, equal to 99·6 per cent. by weight of alcohol. Alcohol mixes with water in all proportions without producing any turbidity; the solution does not affect litmus paper. It must be free from smell, other than that peculiar to alcohol. B.p. of the 100 per cent. alcohol, 78·4° C.

Note.—On the sp. gr. of pure alcohol and its mixtures with water, see a paper by Squibb ("Zeit. f. anal. Chem.," 1887, p. 94; also the alcohol tables in Allen's "Comm. Organ. Anal.," vol. i., p. 95 *et seq.*). According to this author, the present figures for the specific gravity are supposed to be too high. It has been pointed out by him that the last traces of water are very difficult to eliminate. Alcohol is exceedingly hygroscopic.

Pictet assumes that alcohol puriss. purified by crystallisation, is perfectly pure and contains 100 per cent.

Tests for Impurities.—*Residue.*—50 gms. must leave no residue on slow evaporation.

Odour, Colour, etc. (Fusel Oil).—10 c.c. of alcohol are mixed with 30 c.c. of water (good spring water is to be preferred) in a slightly conical glass flask, and this mixture is tested at once for smell, taste, colour, and transparency. It must not show any colour, and no smell other than that peculiar to ethyl alcohol, and must have only a slightly burning taste (neutral).

Note.—An important part of the examination for the purity of an alcohol is the test regarding its odour. The method of testing as

mentioned above, is very satisfactory (see report of the annual meeting of the Association of Swiss Analytical Chemists, in "Chem.-Ztg.," 1893, No. 84). It is very easy in that way for those with some experience to distinguish between inferior and good alcohol. Many technical men test for fusel oil by rubbing a few drops between the hands. It may be remarked here that the strength of the so-called fusel oil smell is not dependent on the quantity of the fusel oil present, but on the presence of certain odorous constituents of the same.

For quantitative estimation of fusel oil, Röse's method (described, *inter alia*, in Böckmann, "Chem.-techn. Untersuchungsmethoden," Springer, Berlin, 1893; "J.S.C.I.," 1886, pp. 393, 498), is the best and the most generally adopted, and is used with various modifications. For the quantitative estimation of small traces of fusel oil in rectified spirit and absolute alcohol by Röse's separation method the modifications introduced by Glasenapp may be advantageously employed. The method is fully described in "Zeit. f. angew. Chem.," 1895, No. 22, p. 657 *et seq.*, and "J.S.C.I.," 1896, p. 140. The presence of a large quantity of fusel oil in commercial spirits of wine can be detected at once by the turbidity formed on diluting with water. Moreover, if, on dilution with a large quantity of water, drops should separate out, it must be observed, according to Bornträger ("J.S.C.I.," 1889, p. 64), whether a smell of acrolein (acetal) is evolved on addition of an equal quantity of concentrated sulphuric acid and caustic potash solution, and if, on adding 3 drops of concentrated hydrochloric acid and 10 drops of colourless aniline oil, a fine raspberry red colour appears (aldehydes).

Aldehyde, etc.—(*a*) 10 c.c. of alcohol are put into a small test tube, and 0·5 c.c. of water and 1 c.c. of a freshly prepared 10 per cent. aqueous solution of meta-phenylene-diamine hydrochloride are added. After one hour's standing there should be scarcely any coloration. (See also note above.)

(*b*) 10 c.c. of absolute alcohol are mixed with 1 c.c. of water, and 5 drops of silver nitrate solution added; this solution must become neither turbid nor coloured on heating.

Note.—The test with meta-phenylene-diamine hydrocloride has been proposed by Windisch, and is also used in the Swiss Excise Department as an important test for impurities peculiar to the first runnings of the distillation, and for acetaldehyde ("J.S.C.I.," 1887, p. 388). The test is based on the fact that meta-phenylene-diamine hydrochloride immediately colours an alcoholic solution containing aldehyde yellow to yellowish-red; then a fine greenish fluorescence appears, which slowly darkens. On comparing the colour reaction so produced with the reactions of solutions containing known quantities of aldehyde the test can be made approximately a quantitative

one. The spirits to be tested are made up at the above-mentioned Excise laboratory to 95 per cent. by volume, and it is required, for example, that the rectified spirit contain not more than 0·1 part by volume of aldehyde per 1000 of alcohol. On long standing even pure absolute alcohol shows a yellow colour, in consequence of formation of aldehyde from oxidation by the air. The meta-phenylene-diamine used for testing must be pure. (See "Meta-phenylene-diamine".)

The test with silver nitrate solution is required by the German Pharmacopœia. Aldehyde must also be tested for by means of ammoniacal silver solution; or with ammoniacal potassium permanganate solution (see "Zeit. f. anal. Chem.," 1891, p. 208, and "Deutsche Medicinische Wochenschrift," 1893, p. 941); further, by means of the fuchsine reaction of Gayon ("J.S.C.I.," 1888, p. 238; also Allen's "Comm. Organ. Anal.," vol. i., p. 159), or with Nessler's reagent. Caustic potash is also used as a test for aldehyde, a yellow colour being produced. It must also be remarked that spirits which have been stored in casks made of wood, containing tannin, show a colour with caustic potash. For the production of an alcohol free from aldehyde, see Paul, "Zeit. f. anal. Chem.," 1896, p. 648.

Foreign Organic Impurities in General.—On mixing 10 c.c. of absolute alcohol with 1 c.c. of water and 1 c.c. of potassium permanganate solution, the red liquid must not become yellow before 20 minutes have elapsed.

Note.—It must be remarked regarding this test, that a partial reduction of the permanganate takes place after 20 minutes, even with the purest alcohol.

Cazeneuve ("J.S.C.I.," 1889, p. 924) observed even after 5 minutes a somewhat yellowish-pink coloration. Since the year 1882 he has taken for comparison chemically pure alcohol of 93° and a potassium permanganate solution of 1 in 1000; 10 c.c. of the pure alcohol require, according to Cazeneuve, 5 minutes at the ordinary temperature to give a rather yellowish-pink colour with 1 c.c. of the permanganate solution, which shows that the reduction is not quite complete. If an alcohol of 93° shows a quicker reduction, this points unmistakably to the presence of impurities. The "Pharm. Ztg." (1889, p. 481) points out that the test with permanganate not only shows the presence of fusel oils, but of every trace of organic matter which originates with the barrels and cork bungs, and is unavoidably present in every alcohol. A slight reduction therefore indicates no occasion for rejection.

Lang (Annual Meeting of the Association of Swiss Analytical Chemists, "Chem.-Ztg.," 1893, No. 84) obtained the following results with the permanganate test. The action of the permanganate test is dependent on the temperature and strength of the spirits, on the more or less complete elimination of the first runnings (these first

runnings have the strongest action on the permanganate), on the time of storing, on the material of the storage vessels (samples of spirit which have been stored for some time in wooden barrels must be distilled before testing with permanganate), on the action of sunlight and various other factors. It is necessary to use caution, and only the following general conclusions can be drawn : inferior spirits show a short period in the oxidation test with permanganate, and the better the sample the longer the duration of the test.

Besides the test with permanganate there is also the sulphuric acid test. On mixing with equal parts of sulphuric acid, no yellow coloration must take place—this is used to detect fusel oils, aldehydes, and other organic compounds ; but according to Glasenapp ("J.S.C.I.," 1895, p. 174), the test is useless for estimating the quality of spirits. Spirits which show no brown colour with sulphuric acid may, under some circumstances, contain more fusel oil than others turning brown. The best quantitative test for fusel oils is, as already remarked, Röse's separation method, as modified by Glasenapp (see p. 10). This method detects even infinitesimal quantities of fusel oils in the best rectified spirits.

Free Acid.—The alcohol after dilution with distilled water must not affect litmus paper.

Note.—Schweissinger ("Rep. d. Chem.-Zeit.," 1887, p. 174) observes that traces of free acid exist in alcohol. According to him 0·4 c.c. $\frac{n}{10}$ soda solution were required to neutralise the free acid in 100 c.c. of a good alcohol. Notwithstanding this, good alcohol must not affect litmus paper. For the estimation of free acid in the Swiss Excise Department ("Chem.-Ztg.," 1893, No. 84) 50 c.c. were titrated with $\frac{n}{20}$ soda solution, using phenolphthalein as indicator. In 1070 analyses it was found that in order to neutralise the acid in 100 c.c. of alcohol the maximum of $\frac{n}{20}$ soda solution used was 3·2 c.c. and the minimum 0·5 c.c.

Methyl Alcohol.—On the detection of methyl alcohol, see E. Aweng, "Apoth. Zeit.," 1912, 27, p. 159 ; "J.S.C.I.," 1912, p. 296).

On the estimation of methyl alcohol in ethyl alcohol, see G. Reif, "J.S.C.I.," 1916, p. 432.

Furfurol.—To 10 c.c. of alcohol 10 drops of aniline oil and 2 or 3 drops of hydrochloric acid are added ; in presence of furfurol a pinkish-red colour is produced more or less deep according to the proportion.

Water.—In most cases, it is sufficient to estimate the amount of water by the specific gravity. To detect very slight traces of water, Léon Crismer's method ("J.C.S.," 1884,

A., p. 1073) is the one generally accepted, which consists in adding a small quantity of the alcohol to a saturated alcoholic solution of liquid paraffin. In the presence of even a small trace of water the liquid becomes at once turbid.

Quantitative Estimation.—The quantitative estimation of alcohol is carried out with the alcoholometer, according to the "Treatise on the Estimation of Alcohol Percentages," as adopted by the German Customs (publ. Springer, Berlin, 1889) or with the Sike's hydrometer for the English Customs, or by estimating the sp. gr. by means of Mohr's balance, and ascertaining the percentage of alcohol equivalent to the sp. gr., according to the following tables (p. 14).

If an accurate estimation of the percentage from the sp. gr. is necessary, so that a tenth per cent. has to be taken into account, reference may be made to Hehner's tables, which are given, *inter alia*, in Muspratt's "Handbuch der technischen Chemie," 4th ed., vol. i., p. 642. It must be remarked here that, according to the article by Squibb (see above), the present figures for the sp. gr. of alcohol are not absolutely correct. As a proof of this assertion, Squibb mentions that, in the manufacture of alcohol on a large scale, by means of very slow filtration through quicklime in the cold, a product of a lower specific gravity is obtained than is mentioned in any other record on the subject. For the quantitative reactions for the estimation of ethyl alcohol, see Klar, "Pharm.-Ztg.," 1896, p. 629.

The per cent. by weight can be found from the per cent. by volume by dividing the sp. gr. of absolute alcohol (according to Gay-Lussac this is 0·7949, and Tralles 0·7939) by the sp. gr. of the alcohol to be tested, and multiplying the quotient by the per cent. by volume of the latter.

Uses and Storage.—Alcohol is used as a solvent, and also for a great variety of purposes in chemical analysis. For some purposes alcohol must be perfectly free from water, as, for example, in the estimation of boric acid by Morse and Burton's method. They used an absolute alcohol, which was freshly distilled over quicklime, and then digested for two or three days with dehydrated copper sulphate ("J.S.C.I.," 1888, p. 525). In connection with alcohol for forensic chemical

analysis, Otto ("Anleitung zur Ausmittelung der Gifte," 1884, p. 105, Brunswick) points out that the ordinary ethyl alcohol of commerce, distilled over quicklime, always contains small quantities of substances of the nature of alkaloids; it must, therefore, before being used for the determination of the latter, be purified once or twice by distillation from a little tartaric acid, which retains the bases.

Specific Gravity and Percentage by Volume of Alcoholic Solutions at 15·56°. Water = 0·9991 (Tralles).

Per Cent. of Alcohol by Vol.	Sp. Gr.	Per Cent. of Alcohol by Vol.	Sp. Gr.	Per Cent. of Alcohol by Vol.	Sp. Gr.	Per Cent. of Alcohol by Vol.	Sp. Gr.
1	0·9971	26	0·9689	51	0·9315	76	0·8739
2	0·9961	27	0·9679	52	0·9295	77	0·8712
3	0·9947	28	0·9668	53	0·9275	78	0·8685
4	0·9933	29	0·9657	54	0·9254	79	0·8658
5	0·9919	30	0·9646	55	0·9234	80	0·8631
6	0·9906	31	0·9634	56	0·9213	81	0·8603
7	0·9893	32	0·9622	57	0·9192	82	0·8575
8	0·9881	33	0·9609	58	0·9170	83	0·8547
9	0·9869	34	0·9596	59	0·9148	84	0·8518
10	0·9857	35	0·9583	60	0·9126	85	0·8488
11	0·9845	36	0·9570	61	0·9104	86	0·8458
12	0·9834	37	0·9559	62	0·9082	87	0·8428
13	0·9823	38	0·9541	63	0·9059	88	0·8397
14	0·9812	39	0·9526	64	0·9036	89	0·8365
15	0·9802	40	0·9510	65	0·9013	90	0·8332
16	0·9791	41	0·9494	66	0·8989	91	0·8299
17	0·9781	42	0·9478	67	0·8965	92	0·8265
18	0·9771	43	0·9461	68	0·8941	93	0·8230
19	0·9761	44	0·9444	69	0·8917	94	0·8194
20	0·9751	45	0·9427	70	0·8892	95	0·8157
21	0·9741	46	0·9409	71	0·8867	96	0·8118
22	0·9731	47	0·9391	72	0·8842	97	0·8077
23	0·9720	48	0·9373	73	0·8817	98	0·8034
24	0·9710	49	0·9354	74	0·8791	99	0·7988
25	0·9700	50	0·9335	75	0·8765	100	0·7939

According to Walter, impure alcohol can be purified for laboratory purposes in the following manner:—

To the alcohol is added as much potassium permanganate solution as will suffice to produce a lasting red coloration. The mixture is allowed to stand for a few hours, so that the manganese oxide which may have formed can settle, and the

liquid is then filtered. A little calcium carbonate is added to the filtrate, which is then distilled slowly so that not more than about 50 c.c. pass over in 20 minutes. The distillate must be tested from time to time, and as soon as 10 c.c. show no signs of yellow coloration after boiling with alcoholic potash, and allowing to stand for half an hour, the remainder of the distillate may be regarded as pure alcohol. Alcohol must be kept in a cool place in well-stoppered bottles.

Commercial Varieties.—Two kinds of absolute alcohol are generally quoted in the price lists, of which one is supposed to be about 99 per cent., and the other from 97 to 98 per cent. strength. For impurities see notes above.

The rectified spirit of commerce of about 93 per cent. is tested like absolute alcohol, and is not to be confused with raw spirits. This rectified spirit, comparatively a very pure alcohol, is manufactured in large refineries from the raw spirit made in distilleries, whereby aldehydes, ketones, and fusel oils are obtained as by-products. Technically, distinction is to be made between prima spirits and secunda spirits, and among these, again, very good, good, and fairly good spirit. The pure varieties stand the above-mentioned practical and other tests, but the less pure varieties differ more or less from the former according to their degree of purity. They show, in particular, the coloration with meta-phenylene-diamine hydrochloride very quickly, and have a disagreeable fusel oil smell. Only comparative tests can be used here with advantage. Good rectified spirit should contain as a maximum equal to aldehyde 0·1 part by volume per 1000. See above notes under "Tests for Aldehyde". The quantitative estimation of fusel oil, according to Glasenapp (see note, p. 10), is also important for the valuation of rectified spirits.

The raw spirits[1] of commerce show a very varying amount of fusel oil, according to the substances from which they were obtained and according as the alcoholic fermentation is more or less pure. Several samples of raw spirits which the author has tested reduced permanganate solution after a few minutes, and immediately gave a colour with the meta-phenylene-

[1] On the testing of commercial spirits and the products of spirit manufacture, see Allen's "Comm. Organ. Anal.," vol. i., p. 143.

diamine test described under "Tests for Aldehyde"; they also gave a yellow colour on mixing with equal parts of sulphuric acid.

Lastly, commercial methylated spirit may be mentioned, which, according to Reinhardt ("J.S.C.I.," 1888, p. 869), is often found to have a very acid reaction, caused by the presence of pyroligneous acid. Bad spirit of this description ruins brass lamps and platinum crucibles, and is therefore not fit to be used for laboratory purposes.

ALCOHOL, METHYL.—Alcohol methylic. puriss. (CH_4O). Mol. wt., 32·03. Clear, colourless liquid, giving no reaction with litmus paper. Mixes in all proportions with water, alcohol, and ether. B.p., 65°. Sp. gr., 0·796.

Tests for Impurities.—*Volatility.*—On evaporating 30 gms. no residue should remain.

Acetone.—10 c.c. of caustic soda solution, with a few drops of iodine solution, are added to 1 c.c. of the alcohol; no turbidity should appear. For the quantitative estimation of acetone, see p. 17.

Caustic Soda Test.—The solution must remain colourless after addition of an indefinite quantity of the soda solution.

Sulphuric Acid Test.—2 c.c. are gradually mixed with 2 c.c. of concentrated sulphuric acid; only a slight yellowish colour, if any, should appear.

Note.—Ordinary methyl alcohol often contains acetone, methyl acetate, methyl acetal, aldehyde, propionic, and allyl alcohol.

The author lately came across a sample marked "puriss." which indicated the presence of a considerable quantity of acetone by the iodoform reaction. Ordinary methyl alcohol shows a decided brown colour with sulphuric acid. On the presence of ethyl alcohol, see "Chem.-Ztg.," 1896, p. 1015.

Boiling Point.—The distillation is conducted in a metallic vessel (see "Acetone," p. 7), and 99 per cent. of the alcohol should distil over within 1° C. See also under "Commercial Varieties".

Quantitative Estimation.—According to G. Krämer and Grodizki, the methyl alcohol present in commercial samples is estimated as methyl iodide, the method being fully described in Allen's "Comm. Organ. Anal.," vol. i., p. 73. For the

detection of methol alcohol, see Trillat ("Analyst," 1899, [24], 13, 211-12).

Note.—Krämer has evolved a method for the quantitative estimation of acetone from a reaction which was first described by Lieben; in this method the methyl alcohol is shaken up with soda and iodine solution in a measuring cylinder, and the iodoform obtained extracted with ether (free from alcohol). A certain quantity of the ethereal solution is evaporated on a tared watch glass, and weighed, the acetone being then calculated from the iodoform obtained ("Ber. d. d. chem. Ges.," xiii., 1000). Hintz ("J.S.C.I.," 1888, p. 459) concludes that this method may be satisfactorily employed where such quantities as may be present in methyl alcohol used by coal-tar manufacturers (from 0·2 to 0·3 per cent.) are concerned, but when a higher percentage of the impurity is present inaccurate results are obtained. He therefore recommends diluting with water when the quantity reaches 5 per cent., till, in the portion taken for analysis, the acetone amounts to from 1 to 1·5 per cent. He advocates the same precaution in the estimation of commercial acetone, loc. cit. Messinger devised later the following volumetric method ("J.C.S.I.," 1889, p. 138): 20 c.c. or, if the sample contains a considerable quantity of acetone, 30 c.c. of normal potash solution, accurately measured, are added to 1 or 2 c.c. of the sample. With pure samples 10 to 15 c.c. of the alcohol may be taken. The mixture is then well shaken in a stoppered bottle, and 20 to 30 c.c. of $\frac{n}{5}$ iodine added from a burette, and again shaken from 15 to 30 seconds until the solution is clear; an equal number of c.c. of hydrochloric acid (sp. gr., 1·025) to the potash solution present is now added, then $\frac{n}{10}$ sodium thiosulphate in excess with some starch indicator, and the solution titrated back with $\frac{n}{5}$ iodine. One equivalent of acetone (58·05) requires six equivalents of iodine (761·52) to form iodoform, hence 1 c.c. equals 0·07615 gm. iodoform.

For the detection of acetone by phenyl hydrazine, see Strache, "J.S.C.I.," 1893, p. 185.

Uses and Storage.—The alcohol is used for the detection of salicylic acid (Curtman, "J.C.S.," 1887, A., p. 185), and further for the estimation of boric acid by Gooch's method ("J.S.C.I.," 1887, p. 385). It is also employed for the preparation of pure grape sugar, and must be kept in a cellar in well-stoppered glass bottles.

Commercial Varieties.—The ordinary methyl alcohol, which contains a small quantity of acetone, is used in the coal-tar colour industry, while a crude form, containing about 90 per cent., can also be obtained. A number of German spirit

manufacturers have adopted the following guarantee for the quality of the better samples :—

(1) Tralles' hydrometer must not show less than 99 per cent. by volume (0·7995 sp. gr.).

(2) The acetone must not exceed 0·7 per cent. by Krämer's method.

(3) At least 95 per cent. must distil over within 1° C.

(4) On admixture with double its volume of 66 per cent. sulphuric acid only a slight yellowish colour must appear.

(5) 5 c.c. must not at once discharge the colour of 1 c.c. permanganate solution, containing 1 gm. per litre.

(6) 25 c.c., when treated with 1 c.c. bromine solution (1 in 80 of 50 per cent. acetic acid), must retain the yellow colour produced.

(7) The methyl alcohol must remain colourless after indefinite additions of concentrated caustic soda solution. Concerning the testing of the commercial varieties, see (particularly) Klar, "Chem. Ind.," 1897, No. 10, p. 218, and "J.S.C.I.," 1897, p. 722.

ALDEHYDE.—Acetaldehyde, CH_3CHO. Mol. wt., 44·04. Colourless liquid. Sp. gr., 0·790. B.p., 21°. Mixes in all proportions with water, alcohol, and ether.

Tests for Impurities.—*Residue.*—It should leave no residue on evaporation. It should not affect litmus paper. The boiling point and specific gravity are sufficient to determine its purity.

Uses and Storage.—It is used in organic synthesis and as a solvent. Owing to its volatility it should be stored in stoppered bottles in a cool place or, better still, in sealed glass flasks. It oxidises in contact with air to form acetic acid.

ALIZARINMONOSULPHONIC ACID.—Alizarine S. (sodium salt of alizarine monosulphonic acid).

This substance has been recommended by F. W. Atack as a reagent for the detection of aluminium, the strength of the solution being 0·1 per cent. To about 5 c.c. of the solution to be tested, which should be neutral or faintly acid, 1 c.c. of the reagent is added and then sufficient ammonia to change the colour to purple, and the mixture boiled for a few minutes,

after which it is acidified with acetic acid. In presence of aluminium there is either a red coloration or precipitate formed. The test is capable of detecting 1 part of aluminium in 10 million parts of water. Phosphates, iron, and chromium do not interfere unless iron is in large amount, while the red salts of Ca, Sr, Ba, Zn, and Mg are dissolved by acetic acid. A process has been devised for estimating aluminium volumetrically by this reagent (F. W. Atack, "J.S.C.I.," 1915, p. 936).

ALKANET TINCTURE.—The alkanet root (*Anchusa tinctoria*) contains a bright red colouring matter which is soluble in alcohol. It is used as an indicator giving a blue colour with alkalies and a red with acids.

MOIST ALUMINA.—Alumina cream, $Al_2(HO)_6$. Mol. wt., 156·25.

Preparation.—A saturated solution of alum in water is prepared. This is divided into two portions one much larger than the other, to the former ammonia in slight excess is added and then the remaining alum solution until the mixture is faintly acid. The result is a fine suspension of alumina in water. This is employed for clarifying sugar solutions previous to estimation by the polariscope and is added in addition to basic lead acetate. (See the latter, p. 169.)

ALUMINIUM.—Aluminium (Al). At. wt., 27·1. Sp. gr., 2·7. Silvery white metal, evolving hydrogen copiously with dilute caustic soda solution, and also with dilute hydrochloric acid.

Aluminium powder is of a light greyish colour.

Note.—Dilute or concentrated sulphuric acid and nitric acid quickly attack and dissolve the pure (about 99 per cent.) aluminium of commerce, according to the investigations of G. A. le Roy ("Bull. Soc. ind. de Rouen," 1891, 19, 232; abst. "J.S.C.I.," 1892, pp. 165, 918).

Tests for Impurities.—See "Quantitative Estimation". Aluminium must contain about 99 per cent. of the metal.

Note.—Tests for arsenic, sulphur, and phosphorus: The hydrogen evolved on treating the metal with pure dilute caustic soda solution must not produce a yellow or a black spot on silver nitrate paper; the hydrogen evolved on using hydrochloric acid must behave likewise (Flückiger, "Arch. d. Pharm.," 1889, p. 17).

With regard to the method of employing this test for arsenic, etc., according to Gutzeit and Flückiger, see "Hydrochloric acid, pure; note on arsenic"; and also the afore-mentioned paper by Flückiger. For the detection of arsenic in other products it would be necessary to employ aluminium which does not respond to the test, but it must be remarked that Flückiger ("Arch. d. Pharm.," 1889, p. 17) could not find a single preparation in the market which was perfectly free from arsenic, sulphur, and phosphorus.

Quantitative Estimation.—In analytical laboratories aluminium is chiefly used in the form of filings for nitric acid estimations. The end to be achieved is therefore to find out the amount by weight of hydrogen which a weighed quantity of the aluminium powder evolves on dissolving in potash solution. The quantity of evolved hydrogen corresponds to the quantity of dissolved aluminium. The latter can be estimated as a check in the alkaline solution, where it exists as potassium aluminate. If this solution is acidified with acetic acid, any zinc dissolved out by the acid solution is easily detected by means of hydrogen sulphide. Particles of iron, which may be present, can be extracted by means of a magnet from the aluminium powder. The method formerly proposed by Klemy for testing aluminium is not accurate, according to Hampe ("Chem.-Ztg.," 1890, No. 97), and also Regensburger ("Zeit. f. angew. Chem.," 1891, p. 360; abst. "J.S.C.I.," 1891, p 387).

In his paper on the estimation of aluminium (loc. cit.) the latter emphasises the point that an impure aluminium can be recognised from various external properties it possesses. The purer the metal the tougher it is, and the further it can be cut without breaking. The cutting so produced has, in the purest qualities, a stringy appearance, with a silky lustre, which becomes more granular and coarsely crystalline according to the amount of iron and silicon present. The principal impurities encountered are, according to Regensburger, iron and silicon (see also further remarks and under "Commercial Varieties"), and he recommends the following process for analysis:—

(1) Silicon: According to the quality of the metal, 2 to 4 gms. of the filings are covered, in a roomy platinum capsule, with 13 to 25 gms. pure potash and about 25 c.c. of warm water, and the mixture left standing with the platinum lid on till

the first strong reaction has somewhat subsided. In order to complete solution, slight heat is then applied, the cover is rinsed with hydrochloric acid and the solution neutralised with acid, stirring all the time. It is then evaporated to dryness with constant stirring on an asbestos bath moistened with strong HCl, and washed with water. The ignited and weighed precipitate is tested with hydrofluoric acid on heating with which it should be entirely volatile.

(2) Iron: To 3 gms. of the filings, in a 500 c.c. flask, are added 50 c.c. of 40 per cent. potash solution; towards the end heat is applied to hasten solution; then with continued shaking 200 c.c. of pure dilute sulphuric acid of about 1·16 sp. gr. are added, and the solution boiled until clear. After cooling for a short time the contents of the flask can be titrated with permanganate, as all the iron is present in the ferrous state.

(3) Aluminium: 2 gms. filings are dissolved in potash solution (12 gms. potash, but a less concentrated solution than that taken at (1)), the solution made up to 200 c.c., and 50 c.c. of the clear solution boiled with about 20 gms. ammonium nitrate, then filtered, washed thoroughly, ignited, and weighed. The precipitate is then finely powdered, and, after being again ignited and cooled, an aliquot part is well boiled with water for the estimation of any alkali which may have been precipitated; another portion is fused in a roomy platinum crucible with dehydrated potassium bisulphate. In the latter operation the precipitated silicic acid remains undissolved on taking up the fused mixture with water, so that its amount can be estimated and taken into account in dealing with the whole precipitate.

(4) Qualitative testing for other metals can be done in the acid filtrate from the silicic acid (1), or in the alkaline solution from (3).

On the estimation of silicon in aluminium, and the estimation of aluminium and its alloys in general, a detailed article by F. Regensburger is also given in "Zeit. f. angew. Chem.," 1891, p. 442; (abst. "J.S.C.I.," 1891, p. 1033).

For more recent communications of a valuable nature on the analytical examination of commercial aluminium, see a

paper by Moissan, "Chem.-Ztg.," 1896, p. 6; "J.S.C.I.," 1896, p. 136.

Uses.—Aluminium is used for the estimation of nitric acid and has also been recommended for the production of hydrogen in testing for arsenic. On the estimation of nitrogen in nitrates by the aluminium process, see Stutzer, "J.C.S.," 1891, A., p. 617.

Aluminium in the form of chips is of special advantage as a reducing agent in alkaline or hydrochloric acid solution; these aluminium chips can be had at a low figure in the market, and contain about 99 per cent. metal. On the analysis of aluminium, and the use of the metal as a reducing agent, see Frank, "J.S.C.I.," 1898, p. 612. On the use of aluminium in the synthesis of aromatic hydrocarbons, see Radziewanowski, "J.C.S.," 1895, A., p. 412. On aluminium amalgam employed as a neutral reducing agent, in presence of water, see Wislicenus and Kaufmann, "J.S.C.I.," 1895, p. 898. They also give the method of preparing aluminium amalgam.

Commercial Varieties.—Aluminium can be obtained in the market in the form of powder, ingot, wire, and foil. Some kinds of commercial aluminium resists the action of soda solution to such an extent that it cannot be used for analytical purposes. (See A. Stutzer, "J.C.S.," 1891, A., p. 617.)

Pure metal manufactured by electrolysis is said to be less active than metal obtained by the old process, which latter often contains much alkali or silicic acid.

Muspratt's "Technische Chemie" quotes analyses which shows percentages of 88 to 97 of pure aluminium in commercial samples. (The remainder according to these analyses consists chiefly of iron and silicon.)

Aluminium for analytical purposes must give a copious evolution of hydrogen with soda or potash solution, and must be as free as possible from arsenic, sulphur, and phosphorus.

The following kinds are to be obtained in the market:—

(1) Pure aluminium (98 to 99·75 per cent.).

(2) Aluminium (92 to 98 per cent.).

G. A. Le Roy ("J.S.C.I.," 1892, p. 166) found on investigating four samples of aluminium had the following composition:—

	Al	Fe	Si
A	98·28	1·60	0·12
B	98·45	1·30	0·25
C	99·60	0·30	0·10
D	99·47	0·40	0·13

According to Moissan ("J.S.C.I.," 1894, p. 1199), commercial aluminium contains iron, silicon, traces of carbon, nitrogen, and alumina. Sometimes, in addition, carbide of boron crystals, and copper.

Moissan has also found ("J.S.C.I.," 1896, p. 204) that commercial aluminium often contains 0·1 to 0·3 per cent. sodium. On boiling these aluminium chips with water, and allowing to stand, solution of the former ensues. The durability of articles made of aluminium is thus very considerably lessened by the presence of sodium, and the homogeneity of the aluminium is often disturbed by foreign admixed particles, such as coal, etc.

On analysis of a sample of aluminium from Pittsburg, Moissan obtained the following figures:—

	Per Cent.
Aluminium	98·82
Iron	·27
Silicon	·15
Copper	·30
Sodium	·15
Carbon	·41
Nitrogen	traces
Titanium	traces
Sulphur	——

AMMONIO-CUPRIC SULPHATE.—This is prepared in solution as a reagent by dissolving 10 gms. of copper sulphate in 100 c.c. of water; ammonia is then added carefully till the precipitate which first forms is just dissolved. The solution is made up to 200 c.c., filtered, and kept in well-stoppered bottles. It is employed for the detection of arsenious acid with which it gives a pale green precipitate.

Note.—Ammonio-cupric sulphate is also employed in volumetric analysis. (See Sutton, 17th ed., p. 50.)

AMMONIO-SILVER NITRATE.—This is prepared in solution as a reagent by dissolving 1 gm. of silver nitrate in 20 c.c. of water, and adding ammonia drop by drop till the precipitate which first forms is nearly dissolved. The liquid is then filtered and kept in well-stoppered bottles. It is used as a reagent for detecting arsenious acid with which it gives a yellow precipitate, soluble in ammonia and in nitric acid.

AMMONIUM ACETATE. — Ammonium aceticum, $NH_4C_2H_3O_2$. Mol. wt., 77·08.

White crystalline mass consisting of deliquescent plates. Very hygroscopic and easily soluble in water, also soluble in alcohol. Loses ammonia on exposure to air and then has an odour of acetic acid.

Tests for Impurities.—*Residue.*—On heating 5 gms. of the material no weighable residue should be left.

Chlorides.—1 gm. dissolved in water and acidified with water should give no opalescence on addition of silver nitrate solution.

Sulphates.—1 gm. dissolved in water and acidified with hydrochloric acid should give no turbidity on addition of barium chloride solution even after standing several hours.

Metals.—5 gms. of the substance dissolved in water should give no coloration with sulphuretted hydrogen. A similar quantity heated with ammonium chloride and ammonia, followed by ammonium sulphide, ammonium oxalate, and sodium phosphate should give no coloration or turbidity.

Uses.—Is employed in the estimation of iron and alumina.

AMMONIUM CARBONATE. — Ammonium carbonicum puriss.: carbonate of ammonia, $NH_4HCO_3 + NH_4(NH_2)CO_2$. A variable mixture of ammonium hydrogen carbonate and ammonium carbamate.

White, hard, fibrous crystalline cakes. Soluble in water (1 : 4).

Tests for Impurities.—*Non-Volatile Matter.*—5 gms. must leave no weighable residue on ignition in a platinum crucible.

Sulphuric Acid.—5 gms. are dissolved in 200 c.c. of water, hydrochloric acid added in slight excess, the liquid heated to

boiling, and barium chloride added. No change should take place even after several hours.

Halogens.—2 gms. are dissolved in 50 c.c. of water, acidified with nitric acid, and nitrate of silver added; no change should take place.

Heavy Metals.—The solution (1 : 20), acidified with acetic acid, should not be coloured by hydrogen sulphide solution.

Note.—A preparation containing iodine and hyposulphate (white or blackish turbidity on adding nitrate of silver) is often met with. The Pharm. Germ. (II.) prescribes a test for iodine, i.e. adding a little chlorine water, acidifying, and shaking up with chloroform. Commercial ammonium carbonate containing zinc has also been met with.

The test for aniline and similar substances is made by evaporating 1 gm. of ammonium carbonate with nitric acid on the water bath: the residue must be white, not yellow.

Quantitative Estimation.—Estimation of residue left on ignition and the other tests given above are sufficient for proving its purity.

In order to test the composition of ammonium carbonate the ammonia is estimated with normal acid, and the carbonic acid by precipitation with barium chloride and ammonia, and the washed barium carbonate estimated alkalimetrically with normal hydrochloric acid and normal alkali solution.

For details of this method, see Sutton's "Vol. Anal.," 7th ed., p. 72.

Uses and Storage.—Carbonate of ammonia is used in the laboratory for precipitating barium, strontium, and calcium, and separating them from magnesium, also for the separation of arsenic sulphide and antimony sulphide. It must be stored in well-stoppered glass bottles as in contact with air it gradually loses both ammonia and carbonic acid.

Commercial Varieties.—A reddish ammonium carbonate is sometimes found in the market, which preparation must not be used for analytical purposes. According to Hager, the quality found in the German trade is generally pure. The ammonium carbonate manufactured in English factories not uncommonly contains iodine. The commercial salt consists chiefly of sesquicarbonate of ammonia which in contact with air quickly loses the normal carbonate, being converted into

bicarbonate of ammonia, a white powdery substance. It is therefore necessary to keep the substance in well-stoppered glass vessels.

Hager remarks that stoneware or clay vessels cannot be used for storing it.

L. L. de Koninck reports as follows on the composition of commercial ammonium carbonate ("Monit. scient.," 1894, 4th series, 8, 420; "Rep. d. Chem.-Ztg.," 1894, p. 175): He dissolved several samples in hydrochloric acid, and titrated the excess of the latter with potash solution, using diazoresorcin as indicator. His results led him to the conclusion that two different commercial products existed. (See also "Zeit. f. anal. Chem.," 1895, p. 598, and Partheil, "Pharm. Ztg.," 1896, p. 650.)

AMMONIUM CHLORIDE.—Chloride of ammonium sal-ammoniac (NH_4Cl). Mol. wt., 53·5. White, hard crystalline lumps, or white, colourless and odourless powdery crystals, consisting of small octohedrons, easily soluble in water (1 : 3). The aqueous solution (1 : 20) must be clear and neutral.

Note.—Even the purest commercial varieties give an acid reaction with litmus in aqueous solution of above proportions.

Tests for Impurities.—*Residue.*—3 gms. must leave no weighable residue after slow volatilisation in a porcelain crucible.

Phosphoric Acid (also arsenic acid).—5 gms. of salt are dissolved in about 30 c.c. of water; the clear solution is mixed with several c.c. of ammonia and magnesia mixture (see under "Magnesium Chloride"); no precipitate must form even after several hours' standing.

Heavy Metals and Earths.—The aqueous solution (1 : 20) must show no reaction with hydrogen sulphide, ammonia ammonium sulphide, or ammonium oxalate.

Note.—The preparation always contains minute traces of iron, and up to the present time the author has not been able to find a sample which gave absolutely no reaction with hydrogen sulphide.

Sulphuric Acid.—The solution (1 : 20) must give no precipitate with barium chloride, even after several hours' standing.

Sulphocyanides.—1 gm. is dissolved in 10 c.c. of water,

and a few drops of hydrochloric acid and ferric chloride added; no red coloration must take place.

Aniline Derivatives.—1 gm. of the salt evaporated to dryness on the water bath with a little nitric acid, must give a white, and not a yellow or reddish, residue.

Quantitative Estimation.—The estimation of ammonia can be made in all ammonium salts by liberating the ammonia with caustic potash solution, passing the gas into an excess of standard acid and titrating back. For a detailed account of this method, see such works on analytical chemistry as Fresenius, "Quantitative Analysis," 7th ed., vol. i., p. 178; and Sutton, "Volumetric Analysis," 7th ed., p 75. The acid in ammonia salts can also be estimated according to well-known methods.

Uses.—Ammonium chloride is used for the precipitation of platinum, and in analytical work it is chiefly employed to retain certain oxides in solution; for example, those of manganese, zinc, and magnesia, or such salts as calcium tartrate, when other oxides or salts are being precipitated with ammonia or other reagents. It is further employed for the preparation of magnesia mixture in the estimation of phosphoric acid (see "Magnesium Chloride"), and is also recommended by Reinitzer as a standard for the estimation of acids, alkalies, and chlorine ("Analyst," 1894, p. 257). For these purposes a very pure preparation may be obtained, according to Reinitzer, by neutralising pure hydrochloric acid with ammonium hydrate (loc. cit.).

Commercial Varieties.—Ammonium chloride is found in the market in the shape of lumps, and as a crystalline powder. Both kinds are obtainable in very different degrees of purity and appearance. The colour of the less pure varieties is grey or yellowish-grey, and they generally contain a large quantity of sulphates, alkalies, earths, and iron. Sulphocyanides are sometimes found in the salt, and chloride of lead has been detected in commercial samples. Only the purest kind should be used for analytical purposes.

AMMONIUM CITRATE.—Formula $(NH_4)_2C_6H_6O_7$. Mol. wt., 226·16.

Tests for Impurities.—*Residue.*—On heating in a platinum dish it should yield no appreciable residue.

Phosphoric Acid.—100 c.c. of the solution should give no precipitate when heated with nitro-molybdate solution.

Uses.—It is employed in the form of a solution in the estimation of citrate soluble phosphoric acid in fertilizers. The solution is prepared as follows: 370 gms. of citric acid are dissolved in 1500 c.c. of distilled water, the solution is nearly neutralised with ammonia and then carefully neutralised with ammonia solution, testing a small quantity with alcoholic solution of corallin from time to time. The liquid is then made up to 2 litres with distilled water. It should have a specific gravity of 1·09 at 20°.

AMMONIUM FLUORIDE.—Ammonium fluoratum puriss.: fluoride of ammonium (NH_4F.) Mol. wt., 37·04. White hexagonal crystals, easily soluble in water, generally showing an acid reaction in consequence of containing the bifluoride.

Tests for Impurities.—See under "Hydrofluoric Acid".

Note.—In a preparation bought as puriss., the author has found nearly 0·5 per cent. of lead. Traces of residue (2 to 3 mgms. on volatilisation of 10 gms.) are nearly always found, and can scarcely be avoided. Nevertheless, a preparation free from lead should certainly be demanded.

Quantitative Estimation.—The ammonia is determined as described under "Ammonium Chloride". For estimation of hydrofluoric acid and ammonium fluoride the salt is dissolved in water, sodium carbonate added in excess, and the whole ignited in a platinum dish till the ammonia is expelled; the residue is dissolved in water and to the clear boiling solution a solution of calcium chloride is added so long as a precipitate forms; after settling, the precipitate, consisting of calcium fluoride and calcium carbonate, is washed, dried, and ignited in a platinum crucible; water is poured over the mass, and a slight excess of acetic acid added. It is then evaporated to dryness, and heated in a water bath till all smell of acetic acid has disappeared. The residue, consisting of calcium fluoride and calcium acetate, is heated with water, the calcium fluoride filtered off, washed, dried, ignited, and weighed. If the ammonium fluoride contains sulphuric acid, the calcium fluoride

obtained during analysis must be tested quantitatively for sulphuric acid. To effect this the precipitate is dissolved in hydrochloric acid, the sulphuric acid precipitated with barium chloride (the solution being previously diluted with water), and the barium sulphate filtered off, ignited, and weighed. From the weight of the latter the quantity of calcium sulphate contained in the calcium fluoride precipitate is calculated, and the amount found deducted from the weight of the latter. The presence of nitric or hydrochloric acids in the aqueous solution of the ammonium fluoride does not interfere with this estimation.

On the quantitative estimation of silicic acid, fluorine, sulphuric acid, chlorine, water, etc., see "Sodium Fluoride".

Uses and Storage.—As under "Hydrofluoric Acid". Ammonium fluoride is kept in vulcanite bottles.

Commercial Varieties.—Commercial ammonium fluoride, usually containing sulphuric acid, is found in the market. The pure preparation cannot always be relied upon without testing.

AMMONIUM HYDRATE.—Liquor Ammon. caustic. pur. (NH_3 + aq.). Mol. wt., NH_3, 17·02. Clear, colourless liquid; sp. gr., ·890, containing 31 to 32 per cent. NH_3.

Tests for Impurities.—*Chlorides* (and pyridine).—10 c.c. diluted with about 30 c.c. of water must remain colourless on acidifying with nitric acid, and the liquid must show no change on addition of nitrate of silver.

Empyreumatic Substances (tar products, pyridine).—On diluting 10 c.c. of ammonia solution with about 30 c.c. of water, and neutralising with dilute sulphuric acid, the liquid must remain odourless.

Note.—Ost recommends the following procedure in testing for empyreumatic substances: 20 c.c. of the ammonia solution are diluted in a beaker with two or three times their bulk of water, one drop of methyl orange is added, then dilute sulphuric acid (1 : 5) is added from a burette; by the aid of the indicator it is easy to detect the point when the ammonia is nearly neutralised, and at that point the odour of the impurities is most sharply defined ("Pharm. Ztg.," 1895, p. 589). This test is very delicate. The test for tar products must, according to Bernbeck ("J.S.C.I.," 1891, p. 164), be conducted

as follows: A layer of the ammonia is poured over crude nitric acid; in presence of tar products a red ring appears at the point of contact. This test is not so sharp as that recommended by Ost.

For the quantitative estimation of pyridine bases in ammonia, Kinzel has worked out a method which is described in the "J.C.S.," 1890, A., p. 1349. Notes on the above methods for the detection of empyreumatic substances are to be found in the "Pharm. Ztg.," 1895, p. 589.

In the literature on the subject it has often been pointed out that commercially pure ammonia solution contains pyridine and pyrrol. The author has found these impurities in samples from various sources, and they are certainly objectionable.

Non-Volatile Matter.—10 c.c. of the ammonia solution must leave no weighable residue on evaporating on the water bath.

Note.—The author has nearly always found traces of residue on evaporation of pure concentrated ammonia solution; these are evidently taken up from the storage vessels.

Metals.—To 5 c.c. are added 20 c.c. of water and a few drops of ammonium sulphide; also another quantity of 5 c.c. is saturated with hydrochloric acid, diluted with 50 c.c. of water, and hydrogen sulphide passed; no change must take place in either test.

Note.—The author has tested liquor ammon. caustic pure, which contained distinct traces of zinc. Stieren mentions in his book an ammonia solution containing copper. Turbid ammonia solution is also sometimes found in the market.

In the "J.S.C.I.," 1892, p. 133, mention is made of a commercially pure ammonia solution containing lead: such an ammonia gives a brown colour on passing hydrogen sulphide. The author has frequently detected lead and even arsenic.

Sulphuric Acid.—10 c.c. are acidified with dilute acetic acid and barium chloride is added; no change should take place, even after standing for a considerable time.

Carbonic Acid.—10 c.c. are mixed with 10 c.c. of water and 20 c.c. of lime water, and the mixture boiled; only a very slight turbidity should appear.

Note.—When ammonia takes up carbonic acid, according to J. Hertkorn ("J.S.C.I.," 1892, p. 457), ammonium carbonate is first formed, which, on boiling the watery solution, is split up into ammonia and carbonic acid. On testing, therefore, for carbonic acid, which may

have been taken up from the air, the liquid should be heated after the addition of the lime water.

Hertkorn considers the test of the German Pharmacopœia (III.) to be wanting in accuracy for the reason that it only prescribes mixing, not boiling, the ammonia solution with lime water.

Quantitative Estimation.—The quantity of ammonia in the solution is found from the specific gravity according to the following notes, which have been taken from the "Pharm. Ztg.," 1889, p. 314:—

The table compiled by Carius was at one time considered the most reliable reference for obtaining the percentage of ammonia from the sp. gr., but in 1882 Messel declared the figures to be inaccurate, and this is borne out by the more recent investigations of H. Grüneberg, and of Lunge and Wiesnick ("J.S.C.I.," 1889, pp. 390, 541), as the results given by these authors, and also Wachsmuth are concordant. The table on page 32 is accurate within + 0·12 per cent. in the higher concentrations, and + 0·25 per cent. in the lower ones.

In using this table the temperatures, taken by an accurate thermometer, must be reduced to 15° by means of the figures for correction in the last column, which give directly the figures to be added or subtracted, but the observed temperature must not be considerably above or below 15°; otherwise the co-efficients of expansion would evidently be different.

For example: Having found the sp. gr. at 13° to be 0·900, in order to find the gr. at 15°, 0·00057 multiplied by 2 must be deducted from that figure, giving roughly 0·899.

Uses and Storage.—Ammonia solution is used very often as a precipitating, separating, and neutralising agent, in quantitative as well as qualitative analysis. It must conform in all respects to the above-mentioned conditions, and must be kept in glass-stoppered bottles in a cool place. This precaution is very essential, as the solution soon loses NH_3 in the summer time if not kept cool.

Commercial Varieties.—In addition to pure ammonia, ammonia for commercial purposes is to be had in the market; both qualities can be procured of various strengths, with a guaranteed sp. gr.

On impurities of ammonia solution, see above notes.

TABLE SHOWING THE STRENGTH OF AMMONIA SOLUTIONS OF VARIOUS SPECIFIC GRAVITIES, BY LUNGE AND WIESNICK.

Sp. Gr. at 15°.	Per Cent. NH_3.	One Litre Contains Gms. NH_3.	Correction of Sp. Gr. for ± 1°.	Sp. Gr. at 15°.	Per Cent. NH_3.	One Litre Contains Gms. NH_3.	Correction of Sp. Gr. for ± 1°.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

Anhydrous ammonia can also be had in iron cylinders, fitted with valves for liberating the gas. On the testing of this anhydrous ammonia, see Lange and Heffter, "J.S.C.I.," 1898, p. 183.

According to H. von Strombeck ("J.S.C.I.," 1892, p. 736) the commercial samples of this so-called anhydrous ammonia contain about 97 to 98·8 per cent. NH_3; the remainder consisting of ammonium carbonate, water, lubricating oil, etc. Strombeck obtains a perfectly pure ammonia by passing the gas over melted metallic sodium and spongy palladium. (For particulars, see loc. cit.)

AMMONIUM MOLYBDATE.—Ammonium molybdaenicum puriss.: molybdate of ammonia $(NH_4)_6Mo_7O_{24}$, $4H_2O$. Mol. wt., 1236·31. Large, colourless six-sided crystals, often showing a greenish shimmer.

Tests for Impurities.—*Phosphoric Acid.*—10 gms. must give a clear solution with 25 c.c. of water and 15 c.c. of ammonia of 0·910 sp. gr. This solution is mixed with 150 c.c. of nitric acid of 1·20 sp. gr., and should then show no yellow precipitate after standing for two hours with slight heat.

Note.—The above-mentioned test is very accurate; to 100 gms. of ammon. molybd. puriss. only 1 mgm. of phosphoric acid (H_3PO_4) was added, when a distinct yellow precipitate was observed on testing in the above way. Most books on analytical chemistry fail to give so exhaustive an account of what may be demanded from molybdenum preparations as that given here and under "Molybdic Acid". When referring to phosphoric acid attention is only generally called to the fact that the molybdic acid solution, prepared for analysis, must be put aside for a few hours at 35° before use, a precaution which, in case of necessity, can easily be observed. On standing for several weeks, the molybdate solution sometimes shows a yellow precipitate, which consists (according to "Zeit. f. anal. Chem.," 1876, p. 290; 1877, p. 52; and 1883, p. 78) of a yellow modification of molybdic acid.

Heavy Metals, etc.—The ammoniacal solution of molybdate of ammonium should show no precipitate on addition of excess of ammonium sulphide; nor should any strong evidence of sulphuric acid or chlorine be apparent on acidifying a solution with nitric acid.

Quantitative Estimation.—The purity of the preparation can be observed superficially from the symmetry of the crystalline formation, and approximately the amount of molybdic acid can be estimated by ignition at a very low temperature in an open platinum dish till the smell of ammonia disappears, and then weighing the residue of MoO_3, which ought to amount to about 81 per cent. For the accurate determination, see under "Molybdic Anhydride".

Uses.—As under "Molybdic Acid". Ammonium molybdate forms a useful test for glue or gelatin with which it yields a white precipitate (E. Schmidt, "Chem. Zeit.," 1910, p. 839).

Commercial Varieties.—These are generally pure white and well crystallised, but they have sometimes a greenish appearance.

AMMONIUM NITRATE.—Ammonium nitricum puriss.: nitrate of ammonia (NH_4NO_3). Mol. wt., 80·05. Colourless crystals, easily soluble in water (2 : 1), causing a marked reduction of temperature, also in alcohol.

Tests for Impurities.—As under "Ammonium Chloride," p. 26.

Quantitative Estimation.—As under "Ammonium Chloride," p. 27.

Uses.—The salt is used in analysis for facilitating the ignition of filter paper, or the combustion of organic substances which are not easily burned; it is also added for the same purpose to ash which is not perfectly freed from carbon. Magnesia mixture, for the estimation of phosphoric acid, is sometimes made with ammonium nitrate, and the salt is further employed in the manufacture of freezing mixtures. In the estimation of sulphur in coke (by Eschka's method), ammonium nitrate perfectly free from sulphur is used for the conversion of the sulphites into sulphates.

Commercial Varieties.—In addition to the pure preparation, the commercial product, sufficiently pure for freezing mixtures, and generally containing decided traces of sulphuric acid, is found in the market.

AMMONIUM OXALATE.—Ammonium oxalicum puriss.: oxalate of ammonia (C_2O_4 $(NH_4)_2$, H_2O). Mol. wt., 142·11. Colourless crystals, soluble in water (1 : 23) to a clear, neutral solution.

Tests for Impurities.—*Solubility.*—See above.

Residue.—3 gms. must leave no weighable residue on ignition in a platinum capsule.

Sulphuric Acid.—5 gms. are dissolved in 200 c.c. of water, and the solution heated to boiling; then a little hydrochloric acid and barium chloride are added; after 12 hours' standing no evidence of sulphuric acid should appear.

Heavy Metals.—The solution (1 : 30) should show no change on addition of ammonia and ammonium sulphide.

Note.—The salt, which is used as a standard in volumetric analysis, must contain 100 per cent. after triturating and drying in the air.

Quantitative Estimation.—This is effected with permanganate, the method being described in this book under "Oxalic Acid," and exhaustively in Fresenius, "Quant. Anal.," 7th ed., vol. i., p. 324. The permanganate solution is standardised on the purest and perfectly dried oxalic acid (*q.v.*) or on potassium tetroxalate.

Uses.—As a test for calcium, see under "Oxalic Acid". Oxalate of ammonium is also used for standardising permanganate solution, and must contain 100 per cent. for that purpose.

Commercial Varieties.—Besides the pure preparation, some kinds containing sulphuric acid, and imperfectly volatile, are to be found; also some with potash salts present. The author has also found free oxalic acid in commercial ammonium oxalate.

AMMONIUM PHOSPHATE.—Ammonium phosphoricum puriss.: acid ammonium phosphate ($(NH_4)_2HPO_4$). Mol. wt., 132·13. White, slightly alkaline, monclinic crystals, gradually losing ammonia on exposure to the air.

Tests for Impurities.—*Arsenic, Nitric Acid, Sulphuric Acid, etc.*—Tests as given under "Sodium Phosphate".

Potassium and Sodium.—The phosphoric acid in 2 gms. of the salt is precipitated with lead acetate. After filtration the excess of lead is precipitated with hydrogen sulphide, the precipitate again filtered off, and the filtrate evaporated to dryness and ignited. If an alkaline residue, soluble in water, is left behind, the presence of potassium or sodium may be inferred.

Uses.—The salt is used in the estimation of magnesia.

Commercial Varieties.—Besides the pure salt, a cheap quality (ammon. phosphoric. crud.) is found in the market, generally strongly contaminated with arsenic and sulphuric acid. It usually shows an acid reaction, in consequence of containing too little ammonia, or it consists wholly of the acid salt $(NH_4)H_2PO_4$ (the ammonium biphosphoric. technic.).

AMMONIUM SULPHATE.—Ammonium sulphuric. puriss.: sulphate of ammonia ($SO_4(NH_4)_2$). Mol. wt., 132·14. Colourless rhombic crystals, easily soluble in water (1 : 1·5).

Tests for Impurities.—*Residue.*—3 gms. must leave no weighable residue on ignition.

Chlorides.—2 gms. are dissolved in 20 c.c. of water; this solution should show no change on addition of nitric acid and nitrate of silver.

Metals.—2 gms. dissolved in 20 c.c. of water must not be affected by hydrogen sulphide, or ammonia and ammonium sulphide.

Sulphocyanides.—1 gm. is dissolved in 10 c.c. of water, and some hydrochloric acid and ferric chloride added; no red colour must appear.

Phosphoric Acid (*and Arsenic Acid*).—The test is conducted as described under "Ammonium Chloride" (see p. 26).

Note.—Samples containing arsenic are often met with in the market; the arsenic can be detected by Marsh's method, and nitric acid may be tested for with indigo solution and sulphuric acid.

For the estimation of organic matter and thiosulphates, see F. J. Lloyd ("Chem. News," 1908, 98, pp. 172-173).

Quantitative Estimation.—The quantitative estimation is made as given under "Ammonium Chloride". The quantitative estimation of sulphate of ammonia, and the other ammonium salts, can be made by estimating the nitrogen by the azotometer—a method adopted in agricultural laboratories (see "Zeit. f. anal. Chem.," 1896, p. 631).

Uses.—The pure salt is chiefly used for the preparation of ferrous ammonium sulphate; further, in analysis, for the precipitation of albuminoids, and separation of the same by Kühne and Chittenden's method (see Allen's "Comm. Organ. Anal.," vol. iv., pp. 342, 469), and for standardising solutions used in the estimation of nitrogen or acids.

Commercial Varieties.—In addition to the pure preparation used for analytical purposes, commercial preparations can be obtained. These are chiefly used for the manufacture of artificial manures, and often have a greenish or bluish colour, and contain arsenic, ferrocyanides, sulphocyanides, iron, and free sulphuric acid.

AMMONIUM SULPHIDE SOLUTION.—Liquor ammon. hydrosulfurat.: sulphide of ammonia solution ($(NH_4)_2S$), formed

by passing SH_2 into a solution of ammonia till saturated, then adding an equal volume of ammonia. Colourless, or only slightly yellow liquid.

Tests for Impurities.—Ammonium sulphide must not show a strong yellow colour, and must give a copious evolution of hydrogen sulphide with acids without formation of a coloured precipitate.

Non-Volatile Matter.—10 gms. must leave no weighable residue on evaporating and heating in a porcelain capsule.

Ammonium Carbonate and Free Ammonia.—On addition of lime and a magnesia salt, no precipitate must be formed, even after heating.

Note.—For the preparation of an arsenic-free ammonium sulphide, see Habbermann, "J.S.C.I.," 1897, p. 466.

Quantitative Estimation.—The H_2S in ammonium sulphide is estimated by titration with permanganate. This method is described in books on volumetric analysis, *inter alia*, Sutton's "Vol. Anal.," 7th ed., p. 330 (see also under "Sodium Sulphide").

Uses and Storage.—Ammonium sulphide is an important group reagent for the detection of metals, and is used in forensic analysis for the detection of hydrocyanic acid. The liquid must be stored in small, well-stoppered bottles. The reagent, on being ordered, must be freshly prepared by the manufacturer. On long-standing, it turns strongly yellow, owing to the formation of polysulphides of ammonium, and ammonium sulphocyanide. Otto ("Ausmittelung der Gifte") warns against the use of ammonium sulphide which has been kept for some time, for the detection of hydrocyanic acid, as it often contains considerable quantities of hyposulphites. If yellow ammonium sulphide has to be used, it must be prepared by dissolving a little sulphur in the colourless or only slightly coloured preparation. The solution of ammonium sulphide is prepared by passing hydrogen sulphide into three parts of ammonia solution till saturated, and then again adding two parts of ammonia solution. On saturating the ammonia solution with hydrogen sulphide, ammonium sulph-hydrate solution is first formed (NH_4SH):—

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

On mixing this again with the same quantity of ammonia solution, a solution of the sulphide is formed—

$$NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$$

If, on the contrary, somewhat less ammonia solution is taken, as recommended above, the ammonium sulphide liquid still contains a little ammonium sulph-hydrate, and this represents the reagent as it is generally used in the chemical laboratory. The ammonium sulph-hydrate solution and the ammonium sulphide solution are colourless, but turn yellow in contact with air, polysulphides being formed—

$$2(NH_4)_2S + O = (NH_4)_2S_2 + 2NH_3 + H_2O.$$

At the same time a part of the sulphur is oxidised to hyposulphurous acid, and on long standing, in contact with air, sulphur is precipitated, the ammonium sulphide solution being eventually converted into an ammoniacal solution of ammonium hyposulphite and sulphur. The ammonium sulphide must, therefore, be kept out of contact with air.

AMMONIUM SULPHOCYANIDE.—Ammonium rhodanatum puriss. : sulphocyanide of ammonia ($CN—S(NH_4)$). Mol. wt., 76·09. Colourless deliquescent plates, easily soluble in water and alcohol.

Tests for Impurities.—*Non-Volatile Matter.*—2 gms. must leave no weighable residue on ignition in a platinum capsule.

Solubility in Alcohol.—1 gm. must dissolve completely in 10 c.c. of alcohol.

Note.—Preparations containing appreciable quantities of chlorides or sulphates are not perfectly soluble in alcohol. On tests for chlorides see "Quantitative Estimation".

Sulphates.—The aqueous solution (1 : 20) must not change within 5 minutes after addition of barium chloride.

Heavy Metals.—The solution (1 : 20) must show neither a precipitate nor a brownish colour after addition of ammonium sulphide.

Iron.—The solution (1 : 20) should remain absolutely colourless after the addition of a little dilute hydrochloric acid (1 c.c. HCl (sp. gr., 1·19) to 10 c.c. of water).

Quantitative Estimation.—Klason and Volhard ("Zeit. f. anal. Chem.," 1879, p. 271, and 1889, p. 619); also Klason ("Chem. News," 1890, p. 37) have shown that it is possible to titrate the soluble sulphocyanides, as accurately as hydrochloric acid, with silver nitrate solution, using potassium chromate as indicator. The solution must be neutral and free from chlorides. Regarding a method by Volhard, according to which it can also be estimated in acid solution with silver nitrate solution, see Sutton's "Vol. Anal.," 7th ed., p. 142. A method for estimating sulphocyanides in presence of chlorides with permanganate is given by Volhard, and improved upon by Klason. Reference should be made to the above-mentioned papers for these methods. Testing for chlorine in presence of sulphocyanides is done, according to Volhard, by dissolving 2 to 3 gms. of the sulphocyanide in 400 c.c. of water, heating on the water bath, and adding nitric acid in small quantities so long as any reaction takes place, i.e. till gas ceases to be evolved. The mixture is left standing on the water bath, the water which has evaporated being replaced from time to time, until a test ceases to give the sulphocyanide reaction with a ferric solution decolorised by nitric acid. Ammonia is then added till alkaline, the solution transferred to a basin, and evaporated to about a third of its bulk on the water bath. The remaining liquid is now free from sulphocyanides and cyanides, and may be tested with silver nitrate solution. Volhard has found that during the process no appreciable amount of chlorine is lost.

Uses.—Ammonium sulphocyanide is used for the detection of iron, and the precipitation of copper ("Rep. d. Chem.-Ztg.," 1889, p. 281), and in volumetric analysis for the estimation of the halogens and of copper and mercury ("Zeit. f. anal. Chem.," 1879, p. 271); for further reference to the estimation of silver, see Sutton's "Vol. Anal.," pp. 142, 298.

Commercial Varieties.—Various qualities of ammonium sulphocyanide can be obtained in the market; even in the purest preparations the author often found traces of iron and lead. The ordinary commercial samples have a yellowish colour, contain empyreumatic substances, and often decided traces of sulphuric acid. For analytical purposes a preparation

showing a fine white colour, and free from the above-mentioned impurities, must be demanded.

ANILINE.—Anilin purum ($C_6H_5NH_2$). Mol. wt., 93·09. Pure aniline is a colourless aromatic liquid, quickly turning brown on exposure to light and air, and is a strong base. It dissolves to a weakly alkaline solution in 31 parts of water, mixes with alcohol and ether in all proportions. Sp. gr. at 15°, 1·026. B.p., 183°.

Tests for Impurities.—The estimation of the boiling point and the specific gravity is sufficient for proving its purity. Pure aniline oil distils over completely between 183° and 184° C.

Quantitative Estimation. — The amount of pure aniline present is determined by the boiling point.

Note.—The impurities of aniline oil consist chiefly of toluidine, the boiling point of which is nearly 200°. Aniline can, therefore, be estimated sufficiently accurately by fractional distillation. Recent detailed notes on the analysis of aniline oils are given by H. Reichardt, "Chem.-Ztg.," 1893, p. 413 *et seq.*; abst. "J.S.C.I.," 1893, p. 954.

Uses and Storage.—By showing certain colorations with oxidising agents, aniline can be used in analysis for the identification of the latter. In consequence, aniline has been introduced as a reagent for nitrates and chlorates. Many other oxidising compounds give reactions with aniline, and the author may here indicate a paper by Laar ("Ber. d. d. chem. Ges.," 1882, p. 2086; "J.S.C.I.," 1883, p. 45), regarding the application of aniline (and diphenylamine) in qualitative analysis. Green and Evershed ("J.C.S.," 1887, A., p. 398; 1892, A., p. 751) use a normal aniline solution for the volumetric estimation of nitrous acid. Aniline is further used in testing for pentoses, furfurol and aldehydes (see under "Alcohol," p. 12). Aniline dissolved in hydrochloric acid colours pinewood yellow, even when diluted 500,000 times. On the colour reactions of aniline with essential oils, see papers by Ihl and Nickel ("J.S.C.I.," 1889, pp. 421, 573). Aniline is used for the detection of chloroform, chloral, bromoform, and iodoform by the isonitrile reaction (A. W. Hofmann). On the detection of woody fibre in paper by means of aniline, see papers by Hanausek and Moeller ("J.S.C.I.," 1887, p. 840).

In microscopy aniline oil is used as a dehydrating and clearing agent (see Bolles Lee's "Microtomist's Vade-Mecum," 4th ed., pp. 70, 109). It should be kept in small bottles protected from light.

Commercial Varieties.—Special distinction is made between four varieties:—

(1) Aniline for blue: Nearly chemically pure aniline.

(2) Aniline for red: A mixture of nearly equal parts aniline, and ortho and para toluidine.

(3) Aniline for safranin is similar to aniline for red, but containing more ortho toluidine.

(4) Liquid toluidine: This consists of a mixture of ortho and para toluidine, and contains only a small quantity of aniline.

For further details as to the testing and properties of aniline, see Schultz, "Chemie des Steinkohlentheers," vol. i., p. 289 *et seq.* (Vieweg, Brunswick, 1886); also Lunge, "Coal Tar and Ammonia," p. 193. In the same reference, also, salts of aniline, aniline hydrochloride (Schultz, p. 302), and the method of testing them are described.

AQUA REGIA.—*Acidum nitrohydrochloricum.*—A mixture of concentrated hydrochloric and nitric acids, usually 4 parts of hydrochloric acid and 1 part of nitric acid. Golden yellow fuming liquid having a powerful odour of chlorine.

Uses.—Aqua regia is employed in dissolving gold, platinum, and some of the more resistant metallic ores. Owing to the fact that it loses strength by spontaneous decomposition it is best prepared when required.

ARSENIOUS ANHYDRIDE. — Acid. arsenicosum pur. (As_2O_3). Mol. wt., 197·92. White lumps, having the appearance of glass or porcelain, or white powder, slightly soluble in water (1 : 31) with acid reaction (arsenious acid, $As(OH)_3$).

Tests for Impurities.—*Residue, and Sulphide of Arsenic.*—1 gm. of the arsenious acid is placed in a small porcelain dish, covered with a porcelain lid or another small dish, and then heated till the arsenious acid begins to sublime. The first coating of arsenious acid must be quite white (free from

sulphide), and on volatilising the rest of the acid by further cautious heating (in a fume closet) no residue should remain.

On arsenious acid for standardising purposes, see under "Uses".

Note.—Great precaution must be taken in performing the above test in consequence of the very poisonous nature of the arsenic fumes. It is also possible to test for volatility in a glass tube, as described in Fresenius, "Quant. Anal.," vol. i., p. 105, but this test can be dispensed with altogether if the acid has been found to contain 100 per cent. of As_2O_3, employing an accurately standardised iodine solution. Sulphide of arsenic may then be detected as follows: 10 gms. are dissolved in caustic soda solution, and 1 to 2 drops of acetate of lead solution added; no brown coloration must appear. According to Hager ("Handbuch der Pharm. Praxis," vol. i., p. 470, J. Springer, Berlin, 1876), As_2O_3 sometimes contains sulphide of arsenic as an impurity, which appears in yellow veins running through the lumps. E. Biltz ("Kritische und praktische Notizen zur Pharm. Germ.," p. 74, publ. Stenger, Erfurt, 1878) has tested (though only on one occasion) the red streaks sometimes pervading the white arsenious acid, for sulphide of arsenic, and was not able to detect it, although he had plenty of material to work upon, but found instead large quantities of oxide of iron.

The testing for sulphide of arsenic and residue is certainly important, as the volumetric solution of arseniate of potash made from it retains its strength only when it contains no trace of sulphur compounds (Mohr's "Lehrbuch der Titrirmethode," publ. by Vieweg, Brunswick, 1886, p. 364).

Quantitative Estimation.—The quantitative estimation is made volumetrically with iodine solution (Sutton's "Vol. Anal.," 7th ed., p. 136; or Fresenius, "Quant. Analysis," vol. i., p. 286).

Note.—Baumann ("J.C.S.," 1893, A., ii., p. 90) recommends a method for the estimation of arsenious acid by means of the azotometer. A weighed quantity of the acid is put into a strongly alkaline solution of ferricyanide of potassium of known strength; the arsenious acid is thus oxidised to arsenic acid, and the ferricyanide is reduced to ferrocyanide. The remainder of the ferricyanide of potassium is then estimated volumetrically. On the above azotometric estimations, see also under "Potassium Ferrocyanide". (For the estimation of arsenic in official medicinal preparations, see Suppl. Rep. to "Pharm. Comm. of Gen. Med. Council," June, 1912; "J.S.C.I.," 1912, p. 748.)

Uses and Storage.—Arsenious acid is used as a standard solution in iodometric analysis, and further, for the detection of

acetic acid. According to Mohr, the best lumps of the commercial acid must be selected for making the standard solution. The preparation used for standardising must be the purest to be had in the market. For the preparation of pure arsenious acid from the commercial product, Friedheim and Michaelis give a very useful method (see "J.S.C.I.," 1895, p. 887) which need only be indicated here. The same authors call attention to the fact that arsenious acid is converted into arsenic acid on allowing the caustic solution of the former to stand, or by the application of heat ("J.C.S.," 1896, A., ii., p. 74). In preparing a standard solution, therefore, heat should not be applied to dissolve the acid in the potash solution. The best method is to dissolve in bicarbonate of potash, in which case oxidation does not take place on heating. Due care must be observed in storing arsenious acid.

AZOLITMIN.—Azolitmin puriss. Thin plates of a dark, reddish-brown colour.

Tests for Impurities.—*Sensitiveness.*—To 100 c.c. of distilled water are added 0·5 c.c. of a slightly alkaline aqueous solution of azolitmin (1 : 100), and the quantity of $\frac{n}{100}$ hydrochloric acid necessary to produce a red colour is then noted, and again the quantity of $\frac{n}{100}$ caustic potash required to produce a distinct blue coloration. On the comparative testing of different indicators by this method, see the table under "Indicators". The azolitmin solution for the above test is made by dissolving 1 gm. of azolitmin in 100 c.c. of water, and adding, drop by drop, $\frac{n}{100}$ alkali solution till a violet tint is reached, or better still, by adding a slight excess of the $\frac{n}{100}$ solution till a distinct blue colour appears, then again acidifying with a few drops of $\frac{n}{100}$ sulphuric acid, and neutralising with $\frac{n}{100}$ alkali solution to a violet tint. Of this solution, 0·5 c.c. is added to 100 c.c. of water (free from carbonic acid), and this quantity should require as little as possible of $\frac{n}{100}$ acid or $\frac{n}{100}$ alkali to produce a distinct change of colour. As the table on "Indicators" shows, a commercial azolitmin (0·5 c.c. of the solution 1 : 100) requires for the above test 1·2 c.c. $\frac{n}{100}$ hydrochloric acid, and 3 c.c. $\frac{n}{100}$ caustic potash. The testing of the azolitmin solution can be conducted advantageously after the

method described under "Litmus Solution"; see also under that heading regarding precautions to be observed.

A good azolitmin should be required to show even a greater degree of sensitiveness, as described in the table under "Indicators"; otherwise its use as an indicator instead of litmus could not be recommended. Trommsdorff, on the other hand, states that he was not able to prepare an azolitmin which was equal to a good litmus solution in sensitiveness (see Böckmann, "Chem-techn. Untersuchung," 3rd ed., vol. i., pp. 119 and 120).

Uses.—Azolitmin is the active principle of litmus; with alkalies it forms easily soluble blue salts (blue colour of litmus). Azolitmin is used as an indicator in solution (1 : 100, prepared as above), and in the form of azolitmin paper. Kretschmer, who gives a method for preparing a tincture of azolitmin, in "Zeit. f. anal. Chem.," 1880, p. 341, has obtained good results with the said tincture. Dietel also highly recommends azolitmin paper. Both used for the preparation the so-called azolitmin sand (see "Zeit. f. anal. Chem.," 1880, p. 341). Azolitmin paper is of a reddish-violet colour, and is obtained by dipping the purest filter paper into a dilute azolitmin solution. It is coloured red by acids, and blue by alkalies. The paper is tested for its degree of sensitiveness to acids and alkalies, as given under "Indicators and Test Papers". The tincture is tested as given above under "Azolitmin Solution 1 : 100," or as under "Litmus Solution" (*q.v.*).

Commercial Varieties.—They are often of inferior quality, according to Trommsdorff's investigations (see above).

Remarks.—According to the investigations of D. R. Brown ("Pharm. Jour. and Trans.," 1896, 56, p. 181) an average of 4·6 per cent. of azolitmin was obtained from several different commercial varieties of litmus. Two of these samples contained as much as 13 per cent.

The amount of insoluble matter varies between 4·6 and 89·8 per cent. Azolitmin is a weak acid, soluble in water and insoluble in alcohol, and a method of preparation is described by the above author.

BARIUM ACETATE.—Barium acetic. puriss. : acetate of

barium ($Ba(C_2H_3O_2)_2,H_2O$). Mol. wt., 273·45. White crystalline powder, easily soluble in water.

Tests for Impurities.—*Halogens.*—1 gm. dissolved in 20 c.c. of water should show no turbidity on addition of silver nitrate solution.

Lime, Alkalies, Heavy Metals, etc.—See under "Barium Carbonate," below.

Quantitative Estimation.—The barium is estimated quantitatively as barium sulphate ($BaSO_4 \times 0{\cdot}58853$) precipitated in acid solution. On the estimation of soluble salts of barium with a solution of sodium carbonate of known strength and titrating the excess, see Sutton's "Vol. Anal.," 7th ed., p. 70; or Clowes and Coleman, "Quant. Anal.," 2nd ed., p. 161.

Acetic acid can be estimated as in all acetates by distillation with phosphoric acid, using a good condenser, and finally titrating with an alkali; volatile acids, however, like sulphurous acid, must not be present. For a full description of a suitable apparatus for that method of estimating acetic acid (in acetate of soda), by G. Neumann, see "J.S.C.I.," 1888, p. 645.

Uses and Storage.—The salt is used in place of barium chloride for the precipitation of sulphuric acid when it is essential to avoid having a chloride in solution, or to convert the base into an acetate. The salt under discussion, as well as all salts of barium, must be carefully stored owing to their poisonous nature.

Commercial Varieties.—Some preparations have a yellow colour, and others contain the chloride; these should be rejected.

BARIUM CARBONATE.—Barium carbonic. puriss.: carbonate of barium ($BaCO_3$). Mol. wt., 197·37. Pure white powder, neutral, soluble, with effervescence, in dilute hydrochloric acid to a clear solution. Almost insoluble in water (1 : 14,000).

Tests for Impurities.—*Lime, Alkalies, etc.*—5 gms. must give a clear solution with a slight excess of dilute hydrochloric acid, and, after diluting this solution with water and heating to boiling, the barium is precipitated with sulphuric acid. After standing several hours the barium sulphate is filtered off. The filtrate must remain clear on mixing with alcohol,

and after evaporating in a platinum dish only slight traces (0·1 to 0·2 per cent.) of mineral matter should remain behind.

Metals, etc.—The solution (1 : 20) must show neither a dark coloration nor a precipitate (after having been previously boiled to get rid of carbonic acid) on addition of hydrogen sulphide, and ammonia and ammonium sulphide.

Barium Chloride or Nitrate.—The solution (1 : 20) in dilute nitric acid should show only a slight turbidity after addition of silver nitrate solution; 1 gm. is dissolved in 10 c.c. dilute acetic acid, a drop of indigo solution, and a few c.c. of concentrated sulphuric acid added; no decoloration should take place.

Quantitative Estimation.—On the estimation of barium, see under "Barium Acetate," and on the volumetric estimation of barium carbonate, see Fresenius, "Quant. Anal.," vol. ii., p. 213.

Uses.—Barium carbonate is used in analysis for the separation of the oxides of iron and alumina from manganous oxide, zinc oxide, lime and magnesia, and for the preparation of other barium salts, etc.

Barium carbonate, absolutely free from chlorine, is used, according to Jaksch, in the estimation of free hydrochloric acid in gastric juice, and is specially prepared for that purpose.

Commercial Varieties.—The preparation is placed on the market in very varying degrees of purity. The ordinary commercial samples are imperfectly soluble in dilute hydrochloric acid, and also contain strong traces of chlorides and nitrates. Barium carbonate, when precipitated from a salt solution with carbonate of potassium or sodium, always contains alkali. For analytical purposes, only the purest kind of barium carbonate —namely, that precipitated with solution of ammonium carbonate—should be used. Native carbonate of barium (witherite) is found in the market, in the form of both lumps and powder.

BARIUM CHLORIDE. — Barium chlorat. puriss. ($BaCl_2$, $2H_2O$). Mol. wt., 244·32. Transparent rhombic crystals, easily soluble in water ($BaCl_2$. 1 : 3), insoluble in concentrated hydrochloric acid. The aqueous solution is clear and neutral.

Tests for Impurities.—*Solubility.*—See above.

Lime, Alkalies, Metals, Nitrates, etc.—See under "Barium Carbonate," p. 45.

Chlorates.—2 gms. are ground to powder, and placed in a test tube along with 10 c.c. concentrated hydrochloric acid. On heating slightly, no yellow coloration of the crystals or solution should appear, and no smell of chlorine.

Quantitative Estimation.—For the estimation of barium, see under "Barium Acetate," p. 45.

Uses.—In the laboratory, barium chloride is used for the separation of acids, and particularly for the detection and estimation of sulphuric acid.

On the preparation of absolutely pure barium chloride (free from strontium and calcium), as used by Richards ("J.C.S.," 1894, A., ii., p. 281; "Chem. News," 1898, pp. 64, 79, 91, etc.) for his atomic weight determinations, see loc. cit. In the aforesaid preparation no trace of calcium or strontium could be found with the spectroscope after very careful fractional separation of the larger part of the barium, and this even held good in working with larger quantities.

Commercial Varieties.—In addition to the pure preparation for analytical purposes, two other varieties exist in the market—viz., barium chlorat. depurat. cryst., and barium chlorat. in the form of powder. The latter preparations often contain iron and have a yellow colour, or are moist in consequence of the presence of calcium. The ordinary commercial salt sometimes contains potassium chloride. The author found up to 15 per cent. of that impurity in inferior qualities, and also met with barium chlorat. depurat. which contained a large quantity of chlorates. Wittstein has found thiosulphate of barium in the commercial varieties. L. Blum ("J.S.C.I.," 1890, p. 766) examined a preparation bought as chemically pure barium chloride which strongly reduced permanganate solution, and which, according to him, contained peroxide of barium.

BARIUM DIOXIDE.—Formula BaO_2. Mol. wt., 169·37. Heavy greyish or yellowish-white powder. Almost insoluble in water.

Tests for Impurities.—*Insoluble Matter.*—5 gms. treated with excess of dilute hydrochloric acid should leave not more than a trace of residue.

Calcium Strontium.—5 gms. treated with excess of dilute hydrochloric acid and the barium precipitated by excess of dilute sulphuric acid, the solution after filtration should show not more than a faint turbidity on addition of ammonia and ammonium oxalate.

Chlorides.—5 gms. treated with dilute nitric acid should on addition of solution of silver nitrate yield not more than a faint turbidity.

Sulphates.—See Insoluble Matter.

Quantitative Estimation.—For this purpose a decinormal solution of permanganate (3·16 gms. per litre) is employed. Two gms. of the material are dissolved in ice-cold water with 7·5 c.c. of phosphoric acid solution. Twenty c.c. of this solution are then titrated with the standard permanganate solution, 1 c.c. of which equals 0·00847 BaO_2. The barium dioxide should contain not less than 80 per cent. of BaO_2.

Uses.—Barium dioxide is used in the preparation of hydrogen dioxide, being suspended in water, and the calculated quantity of sulphuric, hydrochloric, or phosphoric acid added.

BARIUM HYDRATE.—Barium hydric. cryst. puriss.: hydrate of barium ($Ba(OH)_2$, $8H_2O$). Mol. wt., 315·51. Pure white quadratic crystals, soluble in water (BaO 1 : 29) with only a slight residue of barium carbonate.

Note.—Instead of being pure white, the crystals met with in commerce as puriss. have sometimes a yellow colour.

Tests for Impurities.—*Chlorides.*—The solution in nitric acid (1 : 30) should show no change on addition of silver nitrate solution, or only a very slight opalescence after a few minutes.

Lime, Strontia, Metals, Alkalies, etc.—As given under "Barium Carbonate" (see p. 45).

Note.—The ordinary commercial varieties often contain heavy metals (lead).

Barium Sulphide.—After adding an excess of hydrochloric acid the solution of the preparation must not smell of hydrogen sulphide, and must show no black precipitate on addition of acetate of lead.

Quantitative Estimation.—Barium hydrate solution (baryta water) may be titrated with normal acid, using litmus as in-

dicator; 1 c.c. of normal acid = 0·15775 $Ba(OH)_2$, $8H_2O$. On the quantitative estimation of impurities, see under "Commercial Varieties".

Uses and Storage.—Barium hydrate is used in analysis for the precipitation of magnesia, the detection of carbonic acid, for eliminating sulphuric and phosphoric acids, for rendering silicates soluble by fusion, for the preparation of standard alkali solution, and the saponification of fats, etc.

On the preparation of the absolutely pure barium hydrate, as used by Richards for his atomic weight determination, see "Chem. News," 1894, p. 79.

For most analytical purposes, a barium hydrate which has been three or four times recrystallised from water is sufficiently pure. The preparation must be kept protected from the atmosphere, as it readily absorbs carbonic acid. Barium salts are *poisonous.*

Commercial Varieties.—See above note.

Barium hydrate for technical purposes can be obtained in large quantities in the market, both crystallised and fused. The author found in such barium hydrate, in addition to metals of the ammonium sulphide group, decided traces of chlorides. Hintz and Weber ("J.S.C.I.," 1891, p. 272) give the following result of an analysis of commercial barium hydrate:—

	Per Cent.
Barium hydrate ($Ba(OH)_2$, $8H_2O$)	94·31
Barium sulphate	0·52
Barium sulphite	0·07
Barium thiosulphate	0·70
Barium carbonate	1·75
Barium sulphide	0·04

For a detailed account of this analysis, see loc. cit.

BARIUM NITRATE.—Barium nitric. puriss.: nitrate of barium ($Ba(NO_3)_2$). Mol. wt., 261·39. Pure white cubic crystals, soluble in water (1 : 14) to a clear neutral solution.

Tests for Impurities.—*Solubility.*—See above.

Chlorides.—The solution (1 : 20) should show no change on addition of silver nitrate.

Lime, Strontia, Metals, Alkalies, etc.—The tests are performed as given under "Barium Chloride".

Quantitative Estimation.—For the estimation of barium, see under "Barium Acetate," p. 45.

Uses.—As given under "Barium Chloride," p. 47.

For the determination of atomic weights, Richards prepared absolutely pure barium nitrate, perfectly free from calcium, strontium, potassium, and sodium, by recrystallising the commercial product seven times.

Commercial Varieties.—The ordinary commercial products, generally used for technical purposes, fail to give a clear solution and often contain lead.

BARIUM OXALATE.—Barium oxalicum (BaC_2O_4, H_2O). Mol. wt., 243·39. White powder.

Tests for Impurities.—*Solubility, Lime, Alkalies, Chlorides, Nitrates, etc.*, are tested for as given under "Barium Carbonate," p. 45. In testing for metals, in hydrochloric acid solution, as given under "Barium Carbonate," no black coloration must appear on addition of hydrogen sulphide, and no precipitate must be formed on addition of ammonia and ammonium-sulphide.

Uses.—H. Schweitzer and E. Lungwitz, who recommend the following prescription, use the preparation for the estimation of potassium. The commercial oxalate of barium often contains carbonic acid, according to the above-named authors ("J.C.S.," 1895, A., ii., p. 245).

For the preparation of a pure product, a boiling solution of barium chloride is added to a boiling solution of ammonium oxalate. The precipitate is filtered, washed, and dried at 100°. This salt contains half a molecule of water of crystallisation.

BARIUM SULPHIDE.—Sulphide of barium: barium sulphuratum (BaS). Mol. wt., 169·43. Hard, sintered lumps, prepared by igniting a mixture of barytes, powdered coal, and common salt.

Method of Testing.—The preparation in contact with dilute hydrochloric acid must evolve a regular current of pure hydrogen sulphide.

Quantitative Estimation.—In factories the barium sulphide in the commercial compound is determined as follows:—

5 gms. of the melted substance are dissolved in water at 50° to 60°, and hydrochloric acid added in slight excess without previous filtration. The whole mixture is filtered into a 500 c.c. flask, and the residue well washed with hot water; after cooling the flask is filled up to the mark, and in 100 c.c. of this solution the barium is precipitated in the usual way. The barium sulphate obtained is calculated to barium sulphide ("Chem.-Ztg.," 1894, p. 67). If the preparation above described, as used for generating hydrogen sulphide, is to be tested quantitatively, it is best to estimate the gas evolved by the acid in the manner described under "Iron Sulphide".

Uses and Storage.—The preparation is a very suitable agent for the generation of pure hydrogen sulphide ("Zeit. f. anal. Chem.," 1888, p. 26). It is very hygroscopic, becoming covered with a white layer of $Ba(OH)_2$ and $Ba(SH)_2$; and it is therefore necessary to keep it in well-stoppered bottles (see also article by Veley, "J.C.S.," 1886, T., p. 369 *et seq.*).

Commercial Varieties.—In addition to the above preparation for analytical purposes, there is present in the market barium sulphurat. techn. or commercial barium sulphide, sold in lumps said to contain from 60 to 70 per cent of BaS.

BENZENE (BENZOL).—Benzol puriss. (C_6H_6). Mol. wt., 78·08. Colourless, mobile liquid, boiling at 79° insoluble in water, mixes with alcohol and ether in all proportions. Solidifies at + 5°. Sp. gr. at 15°, 0·884.

Tests for Impurities.—*Thiophene.*—On shaking benzol with concentrated sulphuric acid no colour must be produced and it should entirely dissolve. To remove thiophene, see F. Heusler, "J.S.C.I.," 1897, p. 131. The pure commercial benzol must distil over within 1°.

The testing of benzol for carbon disulphide can easily be done quantitatively by Leibermann and Seyewetz' method (see under "Commercial Varieties") by adding 4 to 5 drops of phenylhydrazine to 10 c.c. of benzol, and allowing it to stand, with repeated shaking, from one to one and a half hours. If the benzol contains 0·2 per cent. carbon disulphide, a thick

precipitate occupies the whole volume of the liquid, and even with 0·03 per cent. it is very perceptible.

Quantitative Estimation.—This is determined by fractional distillation. It should commence to distil at 80° C., and at least 90 per cent. of it should pass over below 100° C. On evaporation in an open dish there should be no residue.

Uses.—Benzol is used as a solvent for resins, fats, iodine, etc., and in forensic analysis it is used, like petroleum ether and amyl alcohol, for the separation of alkaloids. Otto ("Anleitung zur Ausmittelung der Gifte," 1884, p. 110, Vieweg, Brunswick) recommends the following procedure for the purification of the solvents mentioned under "Petroleum Ether": That portion of commercial petroleum ether with the lowest boiling point (about 50° C.) should be used. This is obtained from a large quantity of the ether, which has been previously well shaken with (1) spirits of wine, (2) aqueous solution of a mixture of sulphuric and tartaric acids, and finally with distilled water. This treatment removes any bases that may be present. The ether is then dehydrated by means of calcium chloride, and distilled fractionally as before. At this point it is advisable to add some olive oil to remove odorous substances. The petroleum ether so prepared volatilises without leaving any odorous residue. For forensic purposes benzol, amyl alcohol, and ethyl alcohol have to undergo the same treatment, in order to purify them from bases the presence of which has frequently been detected in these liquids.

Benzol from benzoic acid, and benzol from coal-tar oil, are both obtainable in the market, and the latter is the one we have referred to as being used for analytical purposes. It is obtained in a very pure state on the large scale under the name of crystallisable benzol by rectifying the so-called 90 per cent. benzol several times. A small trace of thiophene, which is still retained by it, may be eliminated by shaking with sulphuric acid. Perfectly pure benzol should not be coloured brown by sulphuric acid, and on shaking with isatine and 30 parts of sulphuric acid it should not give a blue solution (Watts' "Dictionary of Chemistry"). On the testing of benzol for thiophene, see "J.S.C.I.," 1888, p. 30.

Commercial Varieties.—The commercial benzol or benzene

is either nearly pure (crystallisable) benzol, C_6H_6 or a mixture of benzol, toluol, xylol, and the hydrocarbons of higher boiling point. It also contains methyl cyanide and hydrocarbons of the methane series. With reference to boiling point, the following commercial varieties are thus differentiated: 30 per cent., 60 per cent., and 90 per cent. according to the amount which distils over below 100° and the so-called crystallisable (chemically pure) benzol described above.

The commercial benzol often contains carbon disulphide, but crystallised benzol has nearly always been found free from this impurity, according to the researches of C. Liebermann and A. Seyewetz ("D. chem. Ges. Ber.," 1891, 24, p. 788; abst. "J.S.C.I.," 1891, p. 578). Many commercially pure benzols (b.p., 80°-82°), supposed to be pure, contained, according to the above observers, 0·2 to 0·3 per cent. carbon disulphide. For further details of commercial varieties and their analysis, see Schultz, "Chemie des Steinkohlentheers," Brunswick, 1886, p. 167.

BENZIDINE.—Paramidophenyl, Diparadiamido diphenyl, $NH_2 . C_6H_4 . C_6H_4NH_2$. White or slightly reddish plates. M.p., 122°. Slightly soluble in water (1 : 2000), slightly soluble in alcohol and ether.

Uses.—Is employed in the estimation of sulphuric acid, benzidine sulphate being only sparingly soluble in water.

Benzidine has also been proposed as a test for blood with which it gives a dark blue colour (Merck's "Annual," 1909, p. 139; 1910, p. 91).

On the estimation of sulphuric acid by means of benzidine, see Raschig ("J.S.C.I.," 1903, 883, 1066).

BENZOIC ACID.—Acidum benzoicum, C_6H_5COOH. Mol. wt., 122·08. White voluminous crystalline plates or needles. M.p., 121°. B.p., 250°. Sparingly soluble in cold water (1 ; 400) but readily soluble in hot water (1 : 45) from which it deposits in crystals almost entirely on cooling. Easily soluble in alcohol and ether.

Tests for Impurities.—*Non-volatile residue.*—Benzoic acid is readily volatile in steam; it is also volatilised by a gentle heat leaving no residue.

Odour.—It should have no odour or only a slight odour of benzoin.

Tests for Salicylic Acid.—A solution of the acid neutralised with ammonia yields a flesh-coloured precipitate with a solution of ferric chloride. There should be no trace of violet colour. The acid can also be distinguished from salicylic acid by the shape of the crystals deposited from boiling water, those of benzoic acid being in thin plates, while the crystals of salicylic acid are long thin needles.

Organic Matter.—A solution in pure sulphuric acid cold should be not deeper than pale brown, and on dilution with water the precipitated acid and the solution should be colourless.

Chlorides.—On heating 1 gm. of the acid with 1·6 gms. of pure calcium carbonate, and dissolving the residue in dilute nitric acid the solution should not give more than a faint opalescence with silver nitrate solution.

Cinnamic Acid.—1 gm. of the acid heated to 45° with 1 gm. of potassium permanganate and 10 c.c. of water for 10 minutes, then stoppering and cooling, should evolve no odour of benzaldehyde.

Oxalic Acid.—1 gm. dissolved in dilute ammonia solution and the excess of the latter evaporated off should yield no precipitate with a solution of calcium chloride.

Hippuric and Cinnamic Acids.—1 gm. dissolved in 50 c.c. of water should not discharge the colour of 10 drops of a 1 per cent. solution of potassium permanganate.

Uses.—Benzoic acid has been suggested as a standard in acidimetry as it can readily be obtained in a very pure state. It must be used with phenolphthalein.

Commercial Varieties.—There are on the market several varieties of benzoic acid. The sublimed acid—*Acidum benzoicum e resina sublimata* is obtained from benzoin resin by sublimation, the *sublimat albiss* and *cryst puriss* being two varieties used for medicinal purposes. *Acidum benzoicum ex urina* is obtained from the hippuric acid of horses' urine by boiling with hydrochloric acid. This is sometimes very pure but usually has a urinous odour. The synthetic benzoic acid—*Acidum benzoicum e toluole*—is obtained from toluene; it usually has a slight odour of benzaldehyde.

BENZOYL PEROXIDE.—Formula,

$$C_6H_5CO \cdot O \cdot O \cdot O \cdot CO \cdot C_6H_5.$$

White crystals. M.p. about 100°.

Uses.—Has been suggested as a test for formaldehyde, with which on adding concentrated sulphuric acid it yields bluish-violet or bluish-green flakes.

It may also be employed as a test for cholesterin (Merck's "Annual," 1909, p. 142).

BISMUTH.—Bismut. metallic. At. wt., 208.

The metal is not often used in the laboratory, and no special tests need therefore be given. For details regarding the analysis of bismuth, see Post, "Chem.-techn. Untersuchungen," 2nd ed., vol. i., p. 619.

The following analyses of two samples of bismuth by R. Schneider are given, along with the methods adopted, in the "Jour. Soc. Chem. Ind.," 1891, p. 1040:—

(1) Refined bismuth from a factory in Saxony, having a yearly output of 18,000 kilograms.

	Per Cent.	Per Cent.
Bismuth . . .	99·791	99·745
Silver	0·070	0·066
Lead	0·084	0·018
Copper	0·027	0·019
Iron	0·017	traces
Sulphur . . .	traces	0·042
Arsenic	none	0·011
Total Cu, Fe, and Pb	0·128	0·037

With the exception of Peruvian bismuth, which contained 2·058 per cent. of copper and iron and 4·57 per cent. of tin and antimony, commercial samples from Saxony, Bolivia, and Joachimsthal, in Bohemia, were always found to contain less than 1 per cent. of foreign matter, the largest quantity present of iron, copper, and lead combined being 0·308 per cent.

(2) Bismuth puriss. Sample (*a*) from Johanngeorgenstadt, obtained by precipitating as protonitrate and reducing to the metallic state, showed 99·922 per cent. of bismuth, 0·016 of

copper, 0·025 of arsenic, and a trace of iron. Sample (*b*), obtained from the basic chloride, gave 99·849 per cent. of bismuth, 0·047 of silver, 0·049 of lead, 0·019 of copper, 0·024 of arsenic, and a trace of iron. Sample (*c*), from Saxony, obtained from the oxychloride, gave 99·892 per cent. of bismuth, 0·065 of lead, 0·032 of copper, and traces of iron and arsenic.

A. Classen (*ibid.*, p. 1041) made similar analyses, but found larger traces of impurities than Schneider. In a sample marked "Bismuth, chemically pure for scientific purposes," and obtained from a well-known factory, a quantity of 500 gms. contained 10 gms. of lead chloride. A similar sample contained 1·56 per cent. of copper and 0·45 per cent. of iron, in addition to lead, which was not estimated. The melting point of absolutely pure bismuth is 264°, but according to Von Aubel a sample labelled "Puriss." obtained from Trommsdorff, melted at 271·8°, another from the same source at 273°, and the absolutely pure metal at from 265°-266°. Schering's bismuth, puriss., melted at from 269°-270°. These facts indicate that some commercial varieties are by no means so pure as they ought to be ("Chem.-Ztg.," 1891, p. 276).

BISMUTH PROTONITRATE.—Bismut. subnitric. puriss.: basic nitrate of bismuth—

$$Bi(NO_3)_3 + (BiH_3O_3)_3. \quad \text{Mol. wt., } 1171{\cdot}75.$$

White, crystalline powder of acid reaction decomposed by water.

Tests for Impurities.—*Arsenic.*—The residue from 1 gm. of the sample, after igniting to drive off the nitric acid, must not show an arsenical mirror on being submitted to Marsh's test for half an hour.

Note.—Regarding various other tests for arsenic, see Flückiger, "J.C.S.," 1889, A., p. 650.

The German Pharmacopœia prescribes the following test: On heating 1 gm. till fumes have ceased to be evolved, and grinding the residue, when cold, the solution in stannous chloride must be colourless. See note under "Iron Chloride," p. 159, for precautions to be observed in testing for arsenic.

Jansen detected a brown colour on testing the carbonate with stannous chloride, which he at first thought to be due to arsenic, but on closer investigation, he found the reaction was caused by tellurium ("Apoth.-Ztg.," 1894, p. 519).

Carbonic Acid, Lead, etc.—On dissolving 0·5 gm. in 25 c.c. of dilute sulphuric acid (1 : 5) in the cold to a clear solution, no carbonic acid must be evolved. A portion of this solution, to which ammonia in excess has been added, must give a colourless filtrate. A second portion, on diluting further, and precipitating with hydrogen sulphide, must give a filtrate which leaves no weighable residue on evaporation.

Chlorides, Sulphuric Acid, and Ammonia.—0·5 gm. dissolved in 5 c.c. of nitric acid must give a clear solution, showing only a slight turbidity on adding 0·5 c.c. of silver nitrate solution, and no reaction with a solution of barium nitrate.

On heating the solution with an excess of caustic soda solution, no ammonia must be given off.

Note.—The two latter tests are taken from the third German Pharmacopœia.

Quantitative Estimation.—The percentage may be roughly estimated by igniting the sample, according to the above Pharmacopœia. 100 parts must leave from 79 to 82 parts of bismuth oxide. The fumes evolved are of a yellowish-red colour.

Uses and Storage.—The salt is used for the preparation of Nylander and Almen's reagent, which consists of a solution of 2 gms. bismuth subnitrate and 4 gms. of Rochelle salt in 100 c.c. of 8 per cent. caustic soda. It is used for the conversion of arsenious and arsenic sulphides into their corresponding acids. Bismuth hydrate is often used for this purpose, and may be tested by the foregoing methods. The subnitrate should be well protected from the air. If the salt turns grey on keeping, silver nitrate is probably present.

Commercial Varieties. — These often contain lead and arsenic.

BLEACHING POWDER.—Calcaria chlorata, Calx chlorinata ($Ca(ClO)_2CaCl_2$, $2H_2O$). Mol. wt., 288. White to whitish powder, smelling of chlorine, soluble in water, leaving a residue of calcium hydrate, and containing at least 30 per cent. available chlorine; becomes moist and decomposes in contact with air, also decomposes even in closed bottles. Slightly soluble in water.

Tests for Impurities.—It is only necessary to estimate the available chlorine.

Quantitative Estimation. — The value of the bleaching powder depends on the amount of available chlorine present. The latter is estimated quantitatively by some of the colorimetric methods; an easy and accurate method is by titration with arsenious acid, comprehensively described in all books on quantitative analysis (see Sutton, "Vol. Anal.," 7th ed., p. 164). A very simple method with the nitrometer using hydrogen peroxide is described by Lunge (Sutton, "Vol. Anal.," 7th ed., p. 165, and "J.S.C.I.," 1890, p. 22).

Uses and Storage. — Bleaching powder is used as an oxidising agent, *inter alia*, for the detection of aniline by Runge's method (see "J.S.C.I.," 1895, pp. 390, 398). In conjunction with hydrogen peroxide it has been recommended by Volhard and Göhring for the convenient preparation of small quantities of oxygen in Kipp's apparatus ("J.C.S.," 1890, A., p. 8), and in the form of hard cakes it is now extensively used for the ready preparation of chlorine in the same apparatus ("Pharm. Ztg.," 1889, p. 641, and Liebig's "Ann. d. Chem.," 1889, pp. 253, 239).

The powder must be kept in well-closed glass or stoneware vessels, in a cool place; through time, loss of available chlorine takes place.

Commercial Varieties.—Commercial bleaching powder is generally sold in degrees Gay-Lussac, and according to that value the 100 per cent. powder should contain 31·8 per cent. chlorine. From these figures it is easy to calculate per cent. to degrees, and *vice versâ*. Gay-Lussac degrees correspond to the litres of chlorine obtainable from 1 kilogram of 90° bleaching powder, therefore 1 kilogram contains 90 litres of available chlorine. The compound loses chlorine on keeping.

BROMINE.—Bromum (Br). At. wt., 79·92. Sp. gr., 2·99. Dark red (almost black) heavy liquid, soluble in 30 parts of water. Gives off red fumes in air.

Tests for Impurities.—*Residue.*—A few grams of bromine spontaneously evaporated in a small porcelain dish must leave no residue.

Sulphur, Iodine, Chlorine, Organic Bromine Compounds (Bromoform, bromides of carbon), etc.—A few grams of the bromine are first converted into bromide of ammonium by adding water and slowly adding excess of ammonia (a clear liquid must be obtained)[1] and evaporating (ammonium bromide is formed by adding 1 part of bromine to 1·5 parts 20 per cent. ammonia solution).

(*a*) *Sulphuric Acid.*—2 gms. of the ammonium bromide, prepared as above, in 60 c.c. of water must give no sulphuric acid reaction with barium chloride.

(*b*) *Iodine.*—When to 1 gm. of the ammonium bromide, dissolved in 10 c.c. of water about 1 c.c. of chloroform is added, a violet colour must not be produced on addition of a few drops of ferric chloride solution.

Note.—Biltz recommends the following simple method, which detects even 1-50th per cent. of iodine, and is also applicable to the testing of hydrobromic acid. The bromine is dissolved in 40 parts of water. Nearly the whole of this solution is shaken up with a sufficient quantity of iron powder for about 1 minute and allowed to settle. The colourless liquid is then transferred to a test tube and starch solution added. On now cautiously adding a few drops of the remaining bromine water, in presence of iodide of iron, a blue ring of iodide of starch will immediately appear below the yellow supernatant liquid. This test may be done as a check.

(*c*) *Chlorine.*—0·1 gm. of the ammonium bromide is dissolved in 10 c.c. of water, and mixed with 4 c.c. of ammonium carbonate solution (1 part of ammonium carbonate and 1 part of ammonia of 0·96 sp. gr. and 3 parts of water); after adding 12 c.c. of $\frac{n}{10}$ nitrate of silver the solution is heated for a short time at 50°-60°; the cooled filtrate should show only a slight opalescence, after acidifying with nitric acid.

Note.—The above test for chlorine is based on the fact that chloride of silver is soluble in warm ammonium sesquicarbonate solution, only traces of bromide of silver being dissolved (iodide of silver being insoluble). A slight opalescence always takes place on acidifying, as silver bromide is not absolutely insoluble, as stated

[1] Organic compounds of bromine slowly separate out as oily drops after adding bromine to ammonia solution. Poselger has found as much as 6 or 8 per cent. of carbon tetrabromide in commercial bromine. Cyanogen has also been detected by T. S. Phipson ("Chem. News," 1873, p. 51).

above, but the presence of 1 per cent. chlorine produces, on acidifying, a strong opalescence, and the filtrate slowly becomes cloudy ("Arch. d. Pharm." 1888, p. 377). A bromine which stands these tests for chlorine is sufficiently pure for most analytical purposes, and should an accurate quantitative estimation be required, methods are described in books on analytical chemistry; but it will very seldom be found necessary, as the bromine marked, "Technically Chlorine Free," and sold by the Bromine Syndicate, at Stassfurt-Leopoldshall, must not contain more than 0·3 per cent. of chlorine, according to the conditions of sale, and is always well within this limit, and containing only a few hundredth parts of a per cent. Good German bromine contains only 0·05 per cent. chlorine, and is free from iodine.

Quantitative Estimation.—The bromine is weighed in a small glass tube, and added to an excess of potassium iodide. The tube is then carefully broken, and the liberated iodine titrated with sodium thiosulphate solution (1 c.c. = 0·008 gm. Br). A more detailed account of this estimation may be found in the textbooks on quantitative analysis (see Fresenius, "Quant. Anal.," vol. i., pp. 361, 365).

For the quantitative estimation of chlorine in bromine, Topf ("Pharm. Ztg.," 1892, p. 364) mentions the following:—

33 c.c. of bromine are shaken in a separator of about 150 c.c. capacity with a little water, and a potassium bromide solution of known strength added; the chlorine dissolved in the water replaces the bromine which separates out, producing turbidity. By carefully adding the above solution and shaking, it is easy to determine accurately the point at which the turbidity ceases to appear, that is, when the chlorine has all been used up. The method is said to be accurate to within 0·03 per cent. In checking the manufacture of bromine in the potash factories the methods of Kubierschky ("J.C.S.," 1891, A., p. 1320) or Erchenbrecher are used. According to the former 25 c.c. of bromine are shaken with 25 c.c. normal potassium bromide solution for about 5 minutes. After settling, 10 c.c. of the supernatant liquid are transferred to a small weighed and well-stoppered bottle, and the weight noted. If the bromine contains no chlorine, the specific gravity of the potassium bromide solution, along with the dissolved bromine, amounts to 1·227. On the contrary, if chlorine is present, the potassium bromide is partially converted into potassium

chloride, and, the gravity is correspondingly lower. In a table specially calculated for this purpose, the amount of chlorine corresponding to the specific gravity can be read off (see "Zeit. f. angew. Chem.," 1894, p. 636).

Uses and Storage.—Bromine is used very largely in analysis as an oxidising agent, and is specially used in the quantitative estimation of sulphur in organic and inorganic substances. Bromine water may be used for the volumetric estimation of phenol.

The alkaline bromine solution, i.e. the solution of sodium hypobromite used for nitrogen estimation in Knop's azotometer, is prepared from bromine and soda solution in the following way: 100 gms. of sodium hydrate are dissolved in $1\frac{1}{4}$ litres of water, and to the cold solution 25 c.c. of bromine are slowly added with agitation.

On the use of gaseous bromine in analysis, see Emmich, "Zeit. f. anal. Chem.," 1893, p. 152, and "J.S.C.I., 1893, p. 711.

Bromine Water—a saturated solution of bromine and water—is obtained by slowly adding bromine drop by drop to distilled water and agitating until bromine ceases to dissolve, which is made apparent by a few drops of bromine collecting at the bottom. This solution is used for identifying the different phenols. A solution of 1 part of bromine and 20 parts of chloroform (Bromchloroform) is used, according to Dragendorff ("Pharm. Ztg.," 1891, p. 725), for the estimation of the ethereal oils of the coniferæ.

Bromine should be stored in a cellar in well-stoppered bottles and is poisonous.

Commercial Varieties.—American and English bromine, according to Hager, are very inferior to German bromine, the latter being of a very pure quality. See note under "Testing for Chlorine," p. 59.

BRUCINE.—Brucinum cryst., pur. ($C_{23}H_{26}N_2O_4$). Small four-sided white prisms, of uncertain hydration ($4H_2O$ or $2H_2O$), which, after dehydrating, dissolve easily in cold alcohol, and are slightly soluble in water, but insoluble in ether and melt at 178°.

Tests for Impurities.—*Strychnine.*—0·5 gm. of brucine (which has been thoroughly dehydrated at 100°) after treat-

ment with 5 gms. absolute alcohol at the ordinary temperature for 1 hour, with occasional shaking, must dissolve completely. If any undissolved strychnine is present the solution is decanted and a portion of the residue placed on a watch glass, allowed to dry, and then dissolved in a few drops concentrated sulphuric acid. A few crystals of potassium bichromate are now added, with gentle agitation; a blue colour, passing through violet and red to green, proves the presence of strychnine, which ought to be entirely absent, or only present in very small traces (Hager).

Dunstan and Short have shown that in a solution of the mixed alkaloids the strychnine is completely precipitated by potassium ferrocyanide (see also Holst and Beckurts, "Pharm. Central.," 1887, p. 119). Brucine can be separated from strychnine by the action of dilute nitric which rapidly destroys the brucine but leaves the strychnine unaffected.

Uses and Storage.—Brucine is very poisonous and must be carefully stored in ribbed bottles. It is used for the detection of nitric acid in potable water. On its use for the estimation of small traces of nitric acid, see Lunge, "J.S.C.I.," 1895, p. 67. According to Lunge and Lwoff (loc. cit.), brucine detects the smallest trace of nitric acid, whereas, contrary to former observations, it gives no reaction with nitrous acid or nitrosyl sulphate.

CADMIUM.—Cadmium metallic puriss. (Cd). At. wt., 112·40. Soft bright metal, with a white lustre resembling tin; melting point, 315.°

Tests for Impurities.—*Tin, Lead, Copper, Zinc, and other Metals.*—1 gm. of the metal is dissolved in nitric acid (tin if present, separating out as oxide), and to 1 part of the solution a large excess of ammonia is added. The solution should remain clear and colourless. The other part is now diluted with water, excess of potash solution added and filtered. The filtrate, even after acidifying with hydrochloric acid, must give no precipitate with hydrogen sulphide.

Quantitative Estimation.—Methods for the separation and estimation of cadmium are described in works on quantitative analysis, e.g., Fresenius, "Quant. Anal.," vol. i., p. 266.

Uses.—According to Whitehead, the metal is used for testing gold previous to minting ("Chem. News," 1891, 64, p. 243).

Commercial Varieties.—The author has often detected large quantities of lead. A guaranteed percentage of 99·75 may be demanded of a good commercial cadmium.

CADMIUM BOROTUNGSTATE SOLUTION.—Heavy yellow liquid.

Tests for Impurities.—It must be a clear, straw-coloured liquid with a sp. gr. of 3·28.

Uses.—It is used in mineralogical examinations for the mechanical separation of mixed minerals.

Commercial Varieties.—Cadmium borotungstate is generally obtained in the market in the liquid form described, but the salt can also be easily prepared in the form of fine large crystals.

CADMIUM IODIDE.—Cadmium iodatum: iodide of cadmium (CdI_2). Mol. wt., 366·24. Bright, transparent, six-sided scaly crystals, resembling mother-of-pearl, easily soluble in water (1 : 1·1) and alcohol.

Tests for Impurities.—Tests are made for other metals as under "Cadmium".

Uses and Storage.—The salt is used for preparing the potassio-iodide of cadmium solution (see appendix), and must be stored in well-stoppered glass bottles.

CALCIUM CARBONATE.—Calcium carbonic. puriss. praec.: carbonate of lime ($CaCO_3$). Mol. wt., 100·07. Pure white crystalline powder (rhombohedrons) slightly soluble in water (1 : 5500).

Tests for Impurities.—*Solubility, Metals, and Magnesia.*—The solution (1 : 50) in dilute hydrochloric acid, must be clear, and must show no precipitate or green colour on adding hydrogen sulphide solution. On adding excess of ammonia to the hydrochloric acid solution, and then precipitating the lime with ammonium oxalate and filtering, no turbidity must appear in the filtrate after addition of sodium phosphate, even after long standing.

Sulphuric Acid and Chlorine.—The solution, in very dilute nitric acid, must show no reaction either with barium nitrate or silver nitrate.

Alkalies.—1 part of calcium carbonate shaken with 50 parts of water must give a filtrate which shows no alkaline reaction, and leaves only traces of residue on evaporation.

Note.—This test is rather too stringent, for this reason, that if ordinary distilled water containing a little carbonic acid is used there will be no reaction, and if the water is boiled there is, in nearly every case, a distinct red coloration with phenolphthalein. This may be due to a slight dissociation of calcium carbonate, which, indeed, is not absolutely insoluble.

Quantitative Estimation.—Lime and carbonic acid are estimated by well-known methods (see Fresenius, "Quant. Anal.," vol. i., p. 185).

Uses.—The purest precipitated carbonate of calcium is used in testing organic compounds for chlorine. Iceland spar is used in making standard hard water for use in water analysis.

Commercial Varieties.—Various kinds of calcium carbonate are found in the market, viz., precipitated calcium carbonate, in varying degrees of purity; in the form of crystals as Iceland spar; in the form of lumps as marble (for the preparation of CO_2); and ordinary carbonate of lime.

Iceland spar is a calcium carbonate of a very high degree of purity, and can be obtained in clear crystalline blocks with a guaranteed percentage of from 99·9 to 100.

An impure calcium carbonate, but sufficiently pure for some laboratory purposes, exists under the name of "Whiting" (ground and washed chalk), and is obtained from the south coast of England and the north of France, and various other places.

CALCIUM CHLORIDE.—Calcium chloratum, crystallisat. puriss.: chloride of calcium ($CaCl_2$, $6H_2O$). Mol. wt., 219·08. Large, clear, transparent, hexagonal crystals, very hygroscopic, easily soluble in water (1 : 1·4).

Tests for Impurities.—*Metals and Sulphuric Acid.*—The aqueous solution (1 : 5) should be clear and neutral, and is tested for other metals with hydrochloric acid and hydrogen sulphide solution, and subsequently ammonium sulphide.

The solution (1 : 20) should show no change, even after several hours, on addition of a few drops of hydrochloric acid and barium chloride.

The salt should dissolve completely in absolute alcohol (1 : 10).

Ammonia.—On boiling 2 gms. with caustic soda solution no ammonia should be evolved; the latter can be detected with moist turmeric paper.

Baryta, etc.—The solution (1 : 20) should show no change, even after long standing, on addition of sulphate of lime solution, and should not turn cloudy on addition of ammonia.

Arsenic.—5 gms. should show no arsenical mirror on applying Marsh's test (see under "Sodium Carbonate").

Quantitative Estimation.—The lime is first precipitated as calcium oxalate, then ignited, and the calcium oxide weighed. Chlorine is estimated as chloride of silver.

Uses and Storage.—Special use is made of this salt for the detection and separation of organic acids, and it must be stored in well-stoppered glass bottles.

Commercial Varieties.—In addition to calcium chloride, pure cryst., the market supplies calcium chloride, pure dry; calcium chloride, pure fused; calcium chloride, crude dry. The latter preparations are used for the drying of gases. The pure dried or fused calcium chloride is white, the raw product has a greyish colour.

CALCIUM OXIDE, FROM MARBLE.—Calcium oxydatum e marmore : quicklime from marble (CaO). Mol. wt., 56·07. Opaque white lumps, evolving much heat on addition of water, and falling to a fine dry powder, slightly soluble in water (1 : 900).

Tests for Impurities.—*Carbonic, Silicic and Sulphuric Acids, Alumina, etc.*—5 gms., on being slaked with 4 parts of water, form a solid mass soluble in dilute hydrochloric acid, with very slight effervescence, and leaving only traces of sand, etc., undissolved. A portion of this solution should show only a slight precipitate of iron and alumina on adding ammonia in excess; another portion tested with barium chloride should give only a slight turbidity.

Quantitative Estimation.—The lime is slaked, dissolved in hydrochloric acid, excess of ammonia added, the solution filtered and precipitated with oxalate of ammonia; the calcium oxalate so obtained is estimated as CaO in the usual way, the filtrate being examined for magnesia. Any carbonic acid which may be present is estimated, either by weight or by volume, in the apparatus described in books on quantitative analysis (see Sutton's "Volumetric Analysis," 7th ed., p. 160).

Uses and Storage.—Lime, as hydrate, is used for expelling ammonia, and in the form of lime water for detecting the presence of carbonic acid, and also in distinguishing between tartaric and citric acids. It is employed in quantitative analysis, in the form of soda lime for the estimation of nitrogen by Will and Varrentrapp's method (the soda lime must be previously tested for nitrogen by a blank experiment with chemically pure sugar).[1]

Purissimum quicklime and soda lime (see under "Calcium Oxide from Iceland Spar") are used for the estimation of sulphur, phosphorous, and chlorine in organic compounds, and blank tests must be made for these elements, as even the purest commercial samples of Calc. oxydat. hydr. e marmore, when tested in large quantity, are not perfectly free from sulphur and chlorine. Quicklime must be stored in well-closed jars or bottles.

Commercial Varieties.—All commercial samples tested by the author showed strong evidence of sulphuric acid, in addition to distinct traces of silica, iron, and alumina. He obtained a purer preparation from Iceland spar crystals.

Bruggelmann, to obtain a preparation free from sulphuric acid for sulphur estimation, ignited the pure calcium nitrate (Fresenius, "Zeit. f. anal. Chem.," vol. xv., p. 185).

Two varieties of commercial quicklime are distinguished as follows: (1) rich or fat lime, (2) poor lime; the latter does not slake so readily as rich lime, this feature being due

[1] It is best to use chemically pure glucose, as, according to Kreusler ("Zeit. f. anal. Chem.," 12, 362), even pure white commercial sugar candy contains 0·012 per cent. nitrogen, and white refined sugar, 0·055 per cent. nitrogen.

either to the presence of magnesia or free or combined silicic acid (clay, silicate of iron).

CALCIUM OXIDE, FROM ICELAND SPAR.—Quicklime from Iceland spar (CaO). Mol. wt., 56·07. Lumps, having the form of Iceland spar crystals.

Note.—Even crystals which externally appear clear and colourless, often contain not inconsiderable traces of iron, and sometimes chloride.

Tests for Impurities.—*Sulphuric Acid.*—3 gms. are dissolved in dilute hydrochloric acid, the solution diluted to 100 c.c., heated to boiling and barium chloride added; after 12 hours' standing, at the most only unweighable and almost imperceptible traces of barium sulphate should appear.

Phosphoric Acid and Chlorine.—3 gms. are dissolved in dilute nitric acid, and tested with silver nitrate and molybdate solution.

Uses, etc.—See the foregoing article.

CALCIUM PHOSPHATE (DICALCIUM PHOSPHATE).—Dibasic phosphate of calcium: calcium phosphoric. puriss. dibasic ($CaHPO_4$, $2H_2O$). Mol. wt., 172·14. Pure white crystalline powder, almost insoluble in water, difficultly soluble in cold acetic acid, soluble in hydrochloric acid to a clear solution without effervescence.

Tests for Impurities.—*Arsenic.*—2 gms. of the salt tested for arsenic in Marsh's apparatus must show no mirror (see under "Sodium Carbonate").

Metals, Chlorides, etc.—2 gms. are dissolved in dilute nitric acid and diluted with water to 40 c.c.; one part of this solution must only show a slight turbidity with silver nitrate, the other portion must give a pure white precipitate on adding excess of ammonia and hydrogen sulphide.

Sulphuric Acid.—On shaking the calcium phosphate with 20 parts of water, acidifying the filtrate with acetic acid, and adding barium nitrate, no precipitate must appear.

On ignition, the salt should lose 25 to 26 per cent.

Note.—To establish the composition of the salt ($CaHPO_4$, $2H_2O$), 1 gm. is carefully ignited in a platinum capsule, dehydrated calcium pyrophosphate ($Ca_2P_2O_7$) being formed, and the loss on ignition is theoretically 26·1 per cent.

Quantitative Estimation.—Phosphoric acid is estimated by the molybdic method (see Sutton's "Volumetric Analysis," 7th ed., pp. 293, 294).

Uses.—It is used as a chemical manure, as is also the dehydrated $CaHPO_4$, the latter being more readily soluble in acetic acid than the hydrated salt.

The above salt, $CaHPO_4$, $2H_2O$, is the preparation required by the German Pharmacopœia, and, according to the latter, must be prepared from the purest material.

Commercial Varieties.—These vary not only in degree of purity, but also in the percentage of water present, the latter depending greatly on the method of precipitating the calcium chloride solution with sodium phosphate.

CALCIUM SUPERPHOSPHATE (DIACID).—Calcium phosphoric. pur. acid: monobasic phosphate of calcium—

$$(CaH_4(PO_4)_2, H_2O). \quad \text{Mol. wt., } 252{\cdot}2.$$

Bright scales, resembling mother-of-pearl, very hygroscopic.

Tests for Impurities, Quantitative Estimation, etc.—The tests are made as described in the foregoing chapter. Small traces of sulphuric acid or free phosphoric acid cannot be regarded as objectionable, as their presence is due to the usual method of preparation. (The salt is prepared by boiling down a solution of the neutral or monoacid salt with hydrochloric, sulphuric, or phosphoric acid.)

CALCIUM PHOSPHATE, NEUTRAL (TRICALCIUM PHOSPHATE).—Calcium phosphoric. puriss. tribasic: tribasic phosphate of lime $Ca_3(PO_4)_2$. Mol. wt., 310·29. Pure white crystalline powder, nearly insoluble in water, easily soluble in hydrochloric and acetic acids without effervescence.

Tests for Impurities.—Tests for arsenic, chlorides, metals, and sulphuric acid are applied as under "Calcium Phosphate," p. 67.

Quantitative Estimation.—By the molybdic method, see under "Dicalcium Phosphate".

Uses.—The natural phosphate or apatite which also contains fluorine is used as a chemical manure. The artificial

variety is obtained by precipitating an ammoniacal calcium chloride solution with disodium phosphate (the dicalcium phosphate described on page 67 is obtained by precipitation from a slightly acid solution). Neutral calcium phosphate is obtained as a gelatinous precipitate, which retains water even after drying *in vacuo*.

Commercial Varieties. — The neutral calcium phosphate occurs native as *phosphorite*, etc., and the precipitated preparation is obtained in commerce in varying degrees of purity, as commercial tribasic phosphate, dry tribasic phosphate, and gelatinous tribasic phosphate.

CALCIUM SULPHATE.—Calcium sulphuricum pur. praec.: sulphate of calcium ($CaSO_4$, $2H_2O$). Mol. wt., 172·16. White crystalline powder (monoclinic), slightly soluble in water (1 : 500).

Tests for Impurities.—*Foreign Substances.*—2 gms. should give a clear solution on heating with 10 c.c. hydrochloric acid and 100 c.c. of water, and no change should take place on warming with ammonia and ammonium sulphide.

The lime is precipitated with oxalate of ammonia, and filtered off. The filtrate ought to leave only slight traces of residue on evaporating and igniting in a platinum dish.

Quantitative Estimation.—A weighed quantity of gypsum is digested with excess of sodium carbonate, filtered, washed, and the calcium carbonate estimated volumetrically with normal hydrochloric acid and normal alkali. In the filtrate the sulphuric acid is estimated with barium chloride in the usual way.

Uses.—Calcium sulphate in solution is used for the detection of oxalic acid, barium, and strontium, and for standardising soap solution for the estimation of the hardness of water.

Commercial Varieties.—The so-called *selenite* is also used for the preparation of sulphate of lime water, and can be obtained in the market. Crude calcium sulphate (ordinary gypsum) is another commercial product. Plaster of Paris is the crude anhydrous sulphate obtained by ignition.

CALCIUM SULPHIDE.—Calcium sulphuratum: sulphide of calcium (CaS). Mol. wt., 72·13. It is used in the form of

small balls, sticks, or lumps for the preparation of pure hydrogen sulphide, free from arsenic. It may be prepared, according to Otto, by igniting a mixture of 7 parts dehydrated gypsum, 3 parts powdered coal, and 1 part of flour. The preparation must evolve a constant stream of pure H_2S in contact with dilute hydrochloric acid.

CARBAZOL.—Diphenylimide $(C_6H_4)_2NH$. Mol. wt., 167·14. M.p., 238°. White or reddish-white plates, sparingly soluble in alcohol.

Uses.—A solution of carbazol in acetic acid is used in the colorimetric estimation of nitrates in water (Sutton "Volumetric Analysis," 17th ed., p. 264).

CARBON DIOXIDE (CO_2).—Mol. wt., 44·00. Evolved by acting upon marble with hydrochloric acid and washing with water. Slightly soluble in water (1 : 1 by volume). The liquefied gas is sold in steel cylinders obtained from breweries. Grünhut ("Chem.-Ztg.," 1895, p. 505, and "J.C.S.," 1895, A., ii., p. 532) has published an elaborate treatise on the testing of liquid carbon dioxide. According to him no gaseous impurities are present, as he always obtained about 100 per cent. on estimation in the eudiometer. Other impurities, however, have often been detected, evidenced by the very disagreeable odour emanating from a liquid which collects at the bottom of the cylinder, sometimes to the extent of 70 gms. in a 10-kilogram bottle. This liquid is brown and turbid, and has generally a sweetish taste. The gas from cylinders containing that impurity colours concentrated sulphuric acid brown, and discharges the colour of very dilute permanganate solution when the gas has been passed for several hours. This test is performed in acid or alkaline solution. The liquid in question contains large quantities of ferric hydrate and glycerine.

On the analysis of liquid CO_2, see Lunge, "Chem. Central.," 1898, vol. i., p. 691.

Storage.—Care must be taken to keep the cylinders in a cool place. Instances of these cylinders exploding are recorded in "Zeit. f. angew. Chem.," 1896, p. 477; also "Chem.-Ztg.," 1896, p. 504.

CARBON DISULPHIDE. — Alcohol sulphuris pur. (CS_2). Mol. wt., 76·12. Sp. gr., 1·272. B.p., 46°-47°. A clear, colourless, highly-inflammable liquid of neutral reaction.

Tests for Impurities.—*Volatility.*—50 gms. must volatilise completely at the ordinary temperature. No brown colour must be imparted to lead carbonate on shaking with the liquid in a separating funnel.

Note.—Carbon disulphide turns yellow under the influence of light. When this occurs a slight residue of sulphur remains on volatilisation. The author, in nearly every case, found traces in commercial samples. The crude variety always contains a large quantity of this impurity, as well as hydrogen sulphide and other sulphur compounds ("Chem.-Ztg.," 1889, p. 627, and "Zeit. f. anal. Chem.," 1879, p. 595).

Quantitative Estimation.—It suffices, as a rule, to determine the boiling point and specific gravity, and to apply the test for sulphur compounds and volatility. On heating a solution supposed to contain carbon disulphide, and passing the gas into a solution of caustic potash in absolute alcohol, a precipitate of potassium xanthate forms; this reaction presents a means of estimating the compound quantitatively (Beilstein, "Handbuch der organ. Chem.," vol, i., p. 722; see also "J.S.C.I.," 1893, p. 293).

Uses and Storage.—It is used as a solvent for fats, resins, iodine, etc., and great care must be taken in handling it, as the vapour, when mixed with air, ignites to form an explosive compound at 150°, even when no naked flame is near. An instance of an explosion of this nature occurring in a palm oil factory is reported in the "Zeit. f. angew. Chem.," 1891, p. 322. See also Max Pöpel ("J.S.C.I.," 1891, p. 787) on spontaneous combustion of carbon disulphide.

Th. Peckolt ("Chem.-Ztg.," 1891, p. 1717) gives an experience he had while analysing the fruit of the *Schinus Terebinthifolius*. He extracted 10 gms. of the fruit with carbon disulphide, and evaporated the extract on the water bath in a porcelain basin, which he kept out of direct contact with the water, on an iron ring. After a short time the carbon disulphide began to boil, and eventually took fire. At first he was under the impression that one of his assistants had ignited phosphorous somewhere in the vicinity, but three subsequent

experiments confirmed the fact that spontaneous combustion had actually taken place.

Commercial Varieties.—The ordinary commercial quality has often a yellow colour. Regarding its impurities, see above.

CARBON TETRACHLORIDE (CCl_4).—Mol. wt., 153·84. A colourless, non-inflammable liquid, of agreeable odour. B.p., 77°. Sp. gr., 1·604°. It is used as a solvent in place of ether, carbon disulphide, etc., and also for extracting and crystallising purposes, also in determining the iodine value. It is insoluble in water, but mixes with alcohol and ether in all proportions. It is not affected by halogens or acids. It should give no reduction with potassium bichromate and sulphuric acid.

CARMINE.—Carmine I. (Naccarat). Fine, light-red compound, obtained from cochineal.

Note.—The manufacture of carmine is kept secret, but from Liebermann's investigations it is known that the fine colour is due to an alumina and lime lake, containing also a protein compound.

Tests for Impurities.—According to Donath ("Dingler's Polyt. Journ.," 1894, vol. 294, p. 188; "J.S.C.I.," 1895, p. 305) cochineal carmine is often adulterated, and not only are the falsifications mentioned on p. 74 possible, but also additions of the lakes of alumina, oxide of tin and baryta, and certain azo compounds, such as Biebrich scarlet and Ponceau scarlet. Referring to the detection of these admixtures, Donath declares that true cochineal carmine is completely soluble in ammonia, whereas the coal-tar dyes above mentioned are insoluble. He further advises the ignition of a small quantity of carmine, known to be genuine, in a small porcelain crucible, side by side with an equal quantity of the carmine to be tested in a second crucible. The odour given off in the decomposition by heat of pure carmine resembles that of proteid substances similarly treated, whereas eosine lake evolves always a smell distinctly like bromine, and peonine lake like phenol, etc. The adulterated samples leave a far larger mineral residue, the method of examining these being given further on.

Note.—For the sake of comparison, a colometric estimation may be made of the various kinds: the simplest way is to place two Nessler glasses of equal dimensions side by side, the one containing the standard solution, and the other the solution to be tested. The stronger coloured liquid is then diluted till the intensity of colour is the same in both. The carmine is dissolved by the aid of ammonia (see under "Ammonia Carmine").

Uses.—It is used in the preparation of carmine stains for microscopical work. The preparation of these stains is exhaustively described in Bolles Lee's "Microtomists' Vade Mecum," 4th ed., p. 145 *et seq.* On the preparation of borax-carmine and ammonia lithium carmine, see above work; also Squire, "Methods and Formulæ," p. 28 *et seq.*

Note.—The following are a few of the carmine stains most frequently used:—

1. **Ammonia Carmine.**—According to Hartig, finely ground commercial carmine is well mixed with water, and ammonia then added drop by drop till the carmine is perfectly dissolved. The solution is filtered and evaporated to dryness; for use, the powder is dissolved in water. According to Bachmann, a carmine solution is easily obtained as follows: 0·2 to 0·4 gm. of carmine is finely ground, and 30 c.c. distilled water, with a few drops of ammonia, added. A part of the carmine is dissolved; the whole is then filtered. If the filtrate smells perceptibly of ammonia, it is allowed to stand exposed to the air till the odour has vanished. To this solution 30 gms. of glycerine and 8 c.c. of alcohol are added.

2. **Borax Carmine.**—4 gms. of borax are dissolved in 56 c.c. of water; to this 1 gm. of carmine is added; 1 part by volume of the whole mixture being mixed with 2 parts by volume of absolute alcohol and filtered.

3. **Grenacher's Alum Carmine.**—A solution of 5 gms. of alum in 100 c.c. distilled water is heated to boiling on a sand bath; then 1 gm. of powdered carmine is added and the mixture boiled for 20 minutes. After removing the flame the mixture is stirred with a glass rod until it attains the ordinary temperature. It is then filtered through good filter paper and kept in a well-stoppered bottle.

4. **Orth's Lithium Carmine.**—Take 100 gms. of a saturated aqueous solution of lithium carbonate, and add 2·5 gms. of powdered carmine, stirring all the time; then filter.

5. **Frey's Picrocarmine** (for histological work).—1 gm. carmine, 4 c.c. ammonia solution, and 200 c.c. distilled water are mixed together, and 5 gms. picric acid added. The mixture is then shaken and decanted, the undissolved picric acid remaining behind. The decanted liquid is allowed to stand a few days, shaking from time to time, and is then poured into a shallow dish and exposed to the air to

evaporate. This takes several weeks, a red powder being left behind, which is then mixed with 50 parts by weight of water, and after standing a few days, filtered. The liquid must now be yellowish-red without smell of ammonia, and a drop placed on white filter paper and evaporated must give a yellow stain with a red edge. The solution is preserved by adding a few drops of carbolic acid.

A tincture, made from cochineal itself, is used as an indicator.

Cochineal Indicator.—According to Lucknow this is prepared by digesting 3 gms. of cochineal for several hours with 250 c.c. of a mixture of three to four volumes of water and one volume of alcohol. Cochineal is preferable to litmus solution, as it gives a good reaction with earthy carbonates in solution where litmus is useless. It gives a yellowish-red colour with acids, and a violet carmine-red colour with alkalies.

The indicator may be used with advantage, for example, in titrating ammonia, or, rather, the excess of sulphuric acid used in nitrogen estimations by Kjeldahl's method. It is well known that phenolphthalein cannot be used in this case. The cochineal indicator keeps well in stoppered bottles.

On cochineal paper, see "Table of Indicators".

The sensitiveness of both paper and indicator is tested against an acid and an ammoniacal solution. On this point, and the estimation of cochineal, see under "Carminic Acid," p. 76.

Red carmine paper is also used in the laboratory, being made by dipping very pure filter paper into an ammoniacal solution of carmine.

Commercial Varieties.—On commercial varieties, see p. 72, under "Tests for Impurities". Carmine is sometimes adulterated with starch, clay, and even brick dust. Donath ("Chem.-Ztg.," 1891, p. 522; also "J.S.C.I.," 1891, p. 758) has examined a large number of samples of carmine, and found two absolute falsifications. One labelled "Ordinary Carmine" had an inferior appearance, was insoluble in ammonia, and the aqueous extract showed the fluorescence of dilute eosine solution. The sample contained 88·5 per cent. of mineral matter on ignition. A hydrochloric acid extract showed the presence of lead oxide and alumina; the residue, insoluble in the acid, consisted of lead sulphate. This compound was an eosine lake

of lead oxide and alumina, mixed with lead sulphate. The sample labelled "Antique Carmine" could scarcely be distinguished superficially from genuine carmine, and had a brilliant appearance. The greater part of it was soluble in ammonia but it contained 74·56 per cent. of ash, chiefly barium carbonate. This sample was evidently a peonine lake.

Genuine samples of carmine (cochineal carmine), according to the investigations of Feitler ("J.S.C.I.," 1893, p. 256), had the following compositions:—

	Cochineal-Carmine, genuine. (Liebermann.)	Cochineal, Naccarat. (Lafar.)	Carmine, finest Naccarat. (Feitler.)	Carmine, finest genuine. (Feitler.)	Carmine, finest genuine. (Feitler.)
Water . . .	17·00	15·50	20·48	13·15	15·69
Ash	7·00	6·87	7·09	9·18	7·24
Nitrogenous substances . .	20·00	23·26	27·00	25·19	20·31
Colouring matter (by difference) . .	56·00	54·37	45·43	52·48	56·36
Analysis of the Ash.					
CuO . . .	traces	0·35	0·45	0·24	1·15
SnO_2 . . .	0·67	0·14	0 62	0·08	1·35
Al_2O_3 . . .	43·09	40·48	35·45	25·95	43·18
Fe_2O_3 . . .	traces	traces	traces	traces	traces
CaO	44·85	44·20	44·98	31·29	36·76
MgO . . .	1·02	0·61	0·81	2·76	1·11
Na_2O . . .	3·23	5·40	5·71	16·24	not estim.
K_2O	3·56	3·20	3·21	1·96	not estim.
P_2O_5 . . .	3·20	2·71	8·31	6·12	1·80
SiO_2 . . .	traces	0·60	0·51	1·65	not estim.
CO_2	—	2·31	—	8·11	not estim.
SO_3	—	—	—	5 14	—
Cl	—	—	—	0·41	—

The finest carmine is termed "Naccarat".

CARMINIC ACID.—Acid carminicum pur. ($C_{22}H_{22}O_{13}$). Mol. wt., 494·29. A purple-brown powder.

Note.—On the preparation of crystallised carminic acid, see "Ber. d. d. chem. Ges.," 1894, p. 2980, paper by Schunck and Marchlewski.

Tests for Impurities.—*Solubility.*—1 gm. should dissolve completely in 2 c.c. of water, and on addition of 20 c.c. of 95

per cent. alcohol to this solution, no appreciable precipitate should be thrown down (see further below).

Quantitative Estimation.—The simplest method for estimating commercial carminic acid is the comparative colorimetric test (see note on p. 73). For use as an indicator, it is important that carminic acid should behave most sensitively towards acid and alkaline solutions. 1 gm. is dissolved in 100 c.c. of water, and 0·5 c.c. of this solution is added to 100 c.c. of water, and the number of c.c. $\frac{n}{100}$ ammonia or hydrochloric acid required to show a change of colour, noted. Its service as an indicator depends upon its degree of delicacy (see Trommsdorff's figures on this point in the tables of indicators).

According to Penny, the carminic acid in cochineal is estimated as follows: 1 gm. cochineal and 5 gms. caustic potash are dissolved in 20 c.c. of water, digested for an hour, and then diluted with water to 100 c.c.; to 10 c.c. of this solution a solution of 1 gm. potassium ferricyanide in 99 c.c. of water is added until the purple colour has disappeared and a yellowish-brown remains. This must be compared with pure carminic acid treated in the same way.

According to Löwenthal ("Zeit. f. anal. Chem.," 1876, p. 179), the colouring capacity of cochineal is determined by permanganate solution. As comparative tests, both methods are said to give good results (see Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 363).

Uses.—Carminic acid is employed as a stain in microscopical work, but for that purpose the commercial carmine is generally used, not the pure carminic acid. The various carmine stains and the cochineal indicator are described in the article on "Carmine," p. 73.

Commercial Varieties.—Under the designation "carminic acid," preparations of a semi-liquid character may be obtained. These give a turbid solution with water and alcohol, and are therefore very impure. The colouring capacity of such commercial preparations varies considerably. With 3 drops of a 0·5 per cent. pure carminic acid solution rendered strongly alkaline, the author was able to impart an intense purple colour to 50 c.c. of water; the same quantity of a sample obtained from a foreign source only coloured the water faintly, and this sample did not dissolve perfectly.

CHARCOAL, ANIMAL.—Carbo animalis puriss. Bulky, dry, black powder.

Tests for Impurities.—*Sulphates, Chlorides, etc.*—1 gm. is boiled for a few minutes with 50 c.c. of water, and the solution filtered. The filtrate must be colourless and neutral, and only show at most a very slight turbidity with silver nitrate or barium chloride. The tests for sulphates and chlorides must show no reaction in 10 c.c. of the solution. On adding 1 drop of indigo solution, diluted with double its volume of water (see p. 148) to 10 c.c. of the solution, and then 5 c.c. of concentrated sulphuric acid, the blue colour must not disappear.

Copper, Iron, Lime, etc.—1 gm. is boiled with 40 c.c. of water and 10 c.c. of hydrochloric acid for a few minutes; no smell of hydrogen sulphide should be detected. The liquid is then filtered through the purest filter paper, and 10 c.c. transferred to a small test tube, in which the solution must appear colourless, must not turn blue on adding ammonia, and must show at most only a slight turbidity with ammonium oxalate, and with ammonium sulphide no precipitate must form, only a slight darkening of the solution being permissible. The solution must produce neither a coloration nor a precipitate with hydrogen sulphide.

Decolorising Power.—This must be from three to four times greater than that of the purest powdered bone black. For this test 1 gm. of the charcoal must be boiled with 10 c.c. of the standard caramel solution (described below) and 50 c.c. of water for a few minutes, after which the solution is filtered. On treating 3 gms. of bone black in the same way, and comparing the filtrates from both tests, that obtained from 1 gm. of the charcoal ought to be at least as much decolorised as the other.

Determination of the Decolorising Power.—Various forms of apparatus have been devised for this most important estimation, particularly for the quality used to such a large extent in sugar factories. Among these special mention may be made of the colorimeters of Salleron and Dubosq. G. Laube gives a simple process for testing bone black used for analytical purposes, but the method may also be used in comparing other kinds of charcoal. According to that author ("J.S.C.I.," 1887,

p. 47) all the pieces which have been burnt white, or have a poor appearance, are removed from the sample, and what remains is then ground to a fine powder, dried at 100°, and kept as a standard. The standard caramel solution [1] is prepared as follows: 50 gms. are dissolved in 50 c.c. of water, 100 c.c. of alcohol added, and the whole diluted to a litre; the solution is allowed to settle for a few days; then filtered and kept. The coefficient is obtained by heating 5 gms. in a flask with 200 c.c. of water to boiling, then adding 10 c.c. of the caramel solution, and after allowing to boil gently for 10 minutes (avoiding evaporation by means of a condenser) the liquid is filtered through a plain double filter. The caramel solution is now added to 200 c.c. of water from a graduated pipette until the same density of colour has been acquired as that shown by the filtrate from the above, the testing being best performed in glass cylinders of the same diameter. If 2·1 c.c. of the standard caramel require to be added to the 200 c.c. of water to produce the same depth of colour, then the charcoal would have decolorised 10 – 2·1 c.c. = 7·9 c.c. When bone black has to be tested, it must be ground to the same degree of fineness as the standard, and is then treated in the same way. If 5 gms. of the standard charcoal decolorise 7·9 c.c., and 5 gms. of bone black 5·5 c.c., then the decolorising power of the latter would be 70 per cent.

Uses.—It is used for analytical purposes as a decolorising agent.

Commercial Varieties. — The charcoal used in analytical work is either the ordinary bone black (the animal charcoal described above, after purification with acid) or purified blood charcoal (carbo sanguinis), which has a particularly strong decolorising power. The various commercial varieties are given in the price lists.

The charcoal should be free from calcium sulphide, an impurity easily detected by the evolution of hydrogen sulphide on adding hydrochloric acid. A further treatment with acid will show whether a sample has been sufficiently digested. The test for sugar is performed by boiling about 200 gms.

[1] Caramel is a thick, dark brown syrup, which may be obtained from liqueur distilleries.

several times with water, and evaporating the extract down to about 30 c.c.; after clarifying with a few drops of lead subacetate, the liquid is examined in the polariscope.

CHLORAL HYDRATE. — Trichloraldehyde. Formula $CCl_3 \cdot CH(OH)_2$. M.p., 57°. B.p., 97°. Soluble in water, alcohol, and ether. Occurs in the form of white moist crystals, it is volatile and has a peculiar characteristic odour. It is an anæsthetic and therefore requires care in handling.

Uses.—It is employed in clearing vegetable tissues for microscopic examination, also as a solvent for gums and certain resins.

CHLORIC ACID.—Acidum chloricum, pur. (ClO_3H). Mol. wt., 84·47. Colourless liquid of 1·20 sp. gr. When concentrated *in vacuo* contains 40 per cent. $HClO_3$.

Note.—Concentrated chloric acid quickly assumes a yellow colour on keeping, in consequence of the liberation of chlorine.

Tests for Impurities.—*Arsenic.*—10 gms of the acid, after diluting with water, are heated with an excess of dilute hydrochloric acid on the water bath till all smell of chlorine has gone. The liquid is then introduced into a Marsh apparatus in small quantities at a time, and tested for arsenic in the usual way.

Baryta.—5 gms. diluted with 50 c.c. of water should only show a slight turbidity with dilute sulphuric acid after standing for a few minutes.

Metals.—3 c.c. are diluted with 10 c.c. of water, and, after addition of hydrochloric acid in excess, evaporated till all smell of chlorine has gone. The residue must give no precipitate either with hydrogen sulphide, or ammonia and ammonium sulphide.

Note.—A slight green colour, on addition of ammonia and ammonium sulphide (traces of iron) need not be objected to.

Quantitative Estimation.—Chloric acid and chlorates decompose on digesting with hydrochloric acid and potassium iodide. The iodine thus liberated may be titrated with decinormal thiosulphate. The method is described in books on

volumetric analysis, e.g., Sutton's "Volumetric Analysis," 7th ed., p. 166; and also under "Potassium Chlorate" in this book.

Uses.—Chloric acid has been recommended by Jeserich for the decomposition of organic compounds, in place of potassium chlorate.

Commercial Varieties.—Chloric acids varying considerably in percentage are placed on the market, and for laboratory purposes the absence of arsenic is absolutely essential; nor must much baryta be present ("Chem.-Ztg.," 1889, p. 275).

CHLORINE AND CHLORINE WATER.—Chlorine (Cl). At. wt., 35·46. A greenish-yellow gas at the ordinary temperature; at − 40°, or under four atmospheres pressure at 15°, it is condensed to a liquid heavier than water, and of a greenish-yellow colour. Liquid chlorine has now been a market article for many years, and is sold in so-called "bombs," steel cylinders, containing 2 kilos.

Chlorine Water.—Aqueous chlorine solution, containing about 2·0 per cent. chlorine.

Note.—The lower the temperature at which this is made the higher the percentage of chlorine absorbed.

Testing and Quantitative Estimation of Chlorine Water.—Chlorine water must be of a pale greenish-yellow colour, and smell strongly of chlorine. It must volatilise perfectly, and such samples as are colourless from decomposition cannot be used.

If 25 gms. of chlorine water are added to 1 gm. of potassium iodide in solution, at least 28·2 c.c. $\frac{n}{10}$ sodium thiosulphate solution must be used to fix the iodine liberated.

Chlorine water must contain 0·4 per cent. Cl, as specified by the German Pharmacopœia.

Storage.—Chlorine water must be kept in a dark cellar, and, as far as possible, in small, well-filled bottles. When the bottles are incompletely filled, or badly stoppered, decomposition takes place, and the solution is soon rendered perfectly useless. In view of its unstable properties, W. Kinzel ("Ber. d. pharm. Ges.," 1894, 4, p. 55) recommends sealing off liquid chlorine in tubes containing 5 gms. for immediate preparation of 1 kilogram of chlorine water.

CHLOROFORM.—Chloroformium, Trichlormethane ($CHCl_3$). Mol. wt., 119·139. Clear, colourless, volatile liquid of peculiar smell. B.p., 61°; sp. gr., 1·490-1·495. Slightly soluble in water (1 : 105), mixes with alcohol and ether in all proportions.

Note.—The boiling point determination has little value so far as estimating the impurities of commercial chloroform is concerned; see J. Brown, "Pharm. Journ. and Transact.," 19th March, 1892.

Tests for Impurities.—*Acidity.*—On shaking 2 parts of chloroform with 3 parts of water, the latter must neither turn blue litmus paper red, nor produce a turbidity on being carefully poured over a solution of silver nitrate in an equal volume of water.

Chlorine.—On shaking with zinc iodide and starch solution, no blue coloration must take place.

Other Chlorine Compounds.—On repeatedly shaking 20 c.c. with 15 c.c. of sulphuric acid in a stoppered bottle (3 c.m. diam.), previously washed with the acid, no coloration must be imparted to the sulphuric acid within an hour.

Note.—In testing for alcohol, De Koninck uses a solution of potassium permanganate in saturated barium hydrate; in the event of alcohol being present, reduction takes place, as shown by the red colour changing to green. Alcohol may also be detected by the green colour developed on adding potassium bichromate and sulphuric acid. Alcohol and ether may be also detected by a lowering of the specific gravity. Several articles on the estimation of chloroform have lately appeared. These have been reviewed in the "Pharm. Ztg.," 1889, p. 29, and also in the last annual volume of that paper.

Quantitative Estimation.—Chloroform may be detected by heating with alcoholic KHO when KCl and potassium formate are produced, also by the production of phenyl isocyanide on heating with aniline and alcoholic KHO. According to Baudrimont, when chloroform is heated with Fehling's solution the following reaction takes place: $CHCl_3 + 2CuO + 5KOH = Cu_2O + 3KCl + K_2CO_3 + 3H_2O$ (Beilstein, "Organ. Chemie"). A method for the volumetric estimation of chloroform is described by L. de Saint-Martin ("Compt. rendus," 106, p. 492; abst. "J.C.S.," 1888, A., p. 570).

Uses and Storage.—Chloroform is used as a solvent for alkaloids, fats, etc., and for the detection of aniline (see the latter), and should be kept in a cool dark cellar, in glass bottles.

The commercial article always contains a little added alcohol to prevent decomposition. That addition need not exceed 0·1 per cent. To purify commercial chloroform from alcohol and water the liquid is shaken with double its volume of concentrated sulphuric acid, neutralised with pieces of potassium carbonate and rectified.

Commercial Varieties.—In addition to the chloroform of the German Pharmacopœia, described above, "Chloroform e Chloral," "Chloroform Pictet," and "Chloroform Anschütz" are found on the market. As a general rule, the commercial samples are of good quality, and the quality prescribed by the above Pharmacopœia is in most cases equal to the very pure chloroform from chloral. "Chloroform Pictet," obtained by crystallisation at – 70°, and below – 100°, is also a very pure preparation. Experiments by Schacht ("J.S.C.I.," 1893, p. 543) show that, although the Pictet Chloroform is a good preparation, that obtained from the purest crystallised chloral hydrate is quite equal to it. Like all the other pure preparations, both decompose if not preserved by the addition of a little alcohol.

During the past few years a special preparation under the name of "Anschütz Salicylide Chloroform" has been placed on the market, which is obtained from a crystalline compound of salicylide, $C_6H_4 \left\{ \begin{matrix} (1)\ CO \\ (2)\ O \end{matrix} \right\}_4$ with chloroform, the resulting compound having the formula, $C_6H_4 \left\{ \begin{matrix} (1)\ CO \\ (2)\ O \end{matrix} \right\}_4, 2CHCl_3$. The preparation was first made by Anschütz ("J.S.C.I.," 1893, p. 782). In this compound chloroform plays the same part as the water of crystallisation in many crystalline salts, and by simple distillation can be obtained in a chemically pure state (E. Merck, "Jahresberichte," 1894).

According to Arends ("Pharm. Ztg.," 1891, p. 263), German chloroform is generally superior to that manufactured in England; this may have been so at that date but is certainly not the case to-day. Some years ago traces of arsenic were found in commercial chloroforms by various experimenters.

CHROMIC ANHYDRIDE.—Acid. chromicum puriss. (CrO_3). Mol. wt., 100. Long, very thin, dry, red needles (rhombic).

M.p., 193°. Soluble in water forming chromic acid (H_2CrO_4), also in dilute alcohol and in pure ether.

Tests for Impurities.—*Sulphuric Acid.*—2 gms. in 20 c.c. of water must give a clear solution, which should show no change within 10 minutes on addition of a few c.c. hydrochloric acid, and a few drops barium chloride solution.

Note.—Commercial samples of chromic acid generally contain a large percentage of free sulphuric acid, or sulphates. Further details are given on this subject by Vulpius in "Arch. d. Pharm.," 1886, p. 965. The above-mentioned pure chromic acid was only brought into the market a few years ago, although prepared for years on a small scale for laboratory purposes, by well-known methods. In testing for sulphuric acid, the chromic acid may first be reduced by heating with alcohol, and then testing with barium chloride (see under "Potassium Bichromate").

Potash Salt.—0·2 gm. of the acid is ignited in a porcelain crucible, and the residue triturated with 20 c.c. of water and filtered. The filtrate, which in all cases of commercial samples has a slight colour, is evaporated to dryness on the water bath, and the residue, which should not exceed 0·002 gm, dried at 200°, and weighed (see Merck's "Annual Report," 1900).

Quantitative Estimation.—Chromic acid and its compounds are estimated either by ferrous-ammonium sulphate or by distillation with hydrochloric acid. In the first method, a solution of ferrous salt is added to the chromate solution containing sulphuric acid, or to the chromic acid alone, until a drop of the liquid shows a blue coloration on being brought into contact with potassium ferricyanide on a white porcelain plate ($CrO_3 = 3FeO$), or the iron salt may be added in the solid state to the chromic acid solution, and the estimation proceeded with as above. The method is described, *inter alia*, in Sutton's "Vol. Anal.," 7th ed., p. 126. In the second method the chromates are distilled with hydrochloric acid, the free chlorine being retained by iodide of potassium solution, and the iodine liberated titrated with $\frac{n}{10}$ thiosulphate solution, after the method described under "Potassium Chlorate". 1 c.c. $\frac{n}{10}$ sodium thiosulphate = 0·004903 gm. $K_2Cr_2O_7$, or 0·00333 gm. CrO_3. An accurate method for the quantitative estimation is described under "Potassium Bichromate". The

poorer qualities of commercial chromic acid often contain considerable quantities of potassium bichromate and potassium sulphate instead of uncombined chromic acid. Under such circumstances an estimation of the sulphuric acid and potash present must be made in order to ascertain the quality of the sample. In testing for potash, etc., the acid is ignited, extracted with water and evaporated; only traces of residue must remain.

Uses and Storage.—Chromic acid, mixed with acetic acid, is employed as an oxidising agent in the decomposition of organic compounds, and also for the same purpose in inorganic analysis. On the estimation of carbon and sulphur by the chromic acid method, see "Zeit. f. anal. Chem.," 1888, p. 463; further "Berl. Ber.," 1888, vol. ii., p. 2910; and on the estimation of phosphorus by chromic acid, see "Chem.-Ztg.," 1887, i., p. 98.

Fresenius ("J.C.S.," 1891, A., pp. 500, 1552; 1892, A., p. 100; "J.S.C.I.," 1892, p. 776) uses chromic acid for the separation of baryta and strontia from lime. Solutions of chromic acid are used in various microscopical investigations, especially for hardening, and for this purpose the preparation must be as pure as possible, and free from sulphuric acid (Frey, "Das Mikroskop," p. 79, publ. by Engelmann, Leipzig).

Chromic acid must be kept in well-closed, glass-stoppered bottles. It is poisonous.

Commercial Varieties.—Besides the above described chromic acid puriss., a pure and a commercial quality are also obtainable, these can be distinguished from the purer variety by reason of their containing sulphuric acid or sulphates, and the bichromates of potash and soda. The author has found over 30 per cent. sulphate of potash in the commercial acid.

CITRIC ACID.—Acid. citricum puriss. ($C_6H_8O_7$, H_2O). Mol. wt., 210·04. Colourless and odourless rhombic crystals, which effloresce and melt on heating. Soluble in 0·5 part of hot and 0·75 part cold water, and in 1·43 parts of boiling alcohol.

Tests for Impurities.—*Oxalic or Tartaric Acid.*—1 gm. of the acid dissolved in 2 c.c. of water must not give a turbid solution on the addition of potassium acetate and alcohol.

An alkaline solution of permanganate gives no reaction with citric acid, but with tartaric acid brown manganese hydroxide is precipitated. A delicate test for tartaric acid is to add 1 drop of a solution of ferrous sulphate, a few drops of hydrogen peroxide, and then an excess of KHO; in presence of tartaric acid a violet coloration is developed.

Sulphuric Acid, Lime, and Metals.—The aqueous solution (1 : 10) must not show any turbidity either on addition of barium chloride solution or ammonium oxalate, or on adding hydrogen sulphide solution after nearly neutralising with ammonia. There should be no odour of burnt sugar, absence of tartaric acid, and no blue colour with K_4FeCy_6.

Lead.—See Tartaric Acid.

Non-Volatile Matter.—1 gm. of the acid must leave no weighable residue on ignition.

Quantitative Estimation.—The acid is titrated with normal alkali solution, using phenolphthalein as indicator; 2 gms. of the crystallised acid, containing 1 molecule H_2O, require 28·5 c.c. normal alkali (see Sutton, "Vol. Anal.," 7th ed., p. 103).

Uses and Storage.—Citric acid is used in the preparation of ammonium citrate solution for the estimation of citrate-soluble phosphoric acid in Thomas' slag. For the preparation of concentrated citrate solution, see Wagner, "J.S.C.I.," 1895, p. 69. One litre of this solution must contain exactly 150 gms. pure crystallised citric acid, and 23 gms. nitrogen as ammonia (27·93 gms. NH_3). The citric acid must be accurately weighed, and the ammonia estimated by analysis.

On the preparation of other citrate solutions, see Wiley's "Agricultural Analysis," vol. ii., p. 57. Citric acid must be kept in well-stoppered glass vessels.

Commercial Varieties.—These often contain lead and sulphuric acid. Citric acid sometimes shows a slight blue colour, which, according to Pusch, is due to the presence of a small quantity of Prussian blue, present as a mechanical impurity (see "Pharm. Ztg.," 1895, No. 76).

COBALT SODIUM NITRITE.—Formula, $Na_6Co_2(NO_2)_{12}$.

This is employed as a delicate test for potassium (Merck's

"Annual," 1912, p. 148). The reagent is prepared by dissolving 220 gms. of sodium nitrite in 400 c.c. of distilled water, and 113 gms. of cobalt acetate in 300 c.c. of water. The two solutions are mixed and 100 c.c. of glacial acetic acid is added. The reagent is then heated and the nitrous fumes which are evolved are allowed to escape, after which the liquid is filtered and made up to 1 litre with distilled water.

On adding this reagent to a solution containing a potassium salt, there is a gradual deposition of the yellow sparingly soluble potassium compound $K_6Co_2(NO_2)_{12} . 3H_2O$ which forms in characteristic microscopic pyramidal or cubic crystals.

COBALTOUS NITRATE.—Cobaltum nitricum, puriss.: nitrate of cobalt ($Co(NO_3)_2$, $6H_2O$). Mol. wt., 290·08. Red, deliquescent crystals (monoclinic) easily soluble in water.

Tests for Impurities.—*Sulphuric Acid.*—The solution (1 : 20) must not show a turbidity with barium chloride.

Lead, Copper, etc.—2 gms. dissolved in 50 c.c. of water with 2 c.c. nitric acid added must show no reaction with hydrogen sulphide water.

Alkalies, Salts, etc.—2 gms. are dissolved in 100 c.c. of water and the cobalt precipitated with ammonia and ammonium sulphide; on evaporating the filtrate to dryness and igniting no weighable residue must remain.

Quantitative Estimation.—The cobalt is precipitated as potassio-cobaltic nitrite. After drying, the precipitate is washed and dissolved in a sufficient quantity of hydrochloric acid, and the cobalt again precipitated with caustic potash, and finally estimated in the metallic state by reduction. In this way the separation of cobalt from nickel is effected (see Fresenius, "Quant. Anal.," vol. i., p. 211). Regarding separation of cobalt from other metals, see *ibid.*, p. 434.

Note.—A criticism on the various methods proposed for the separation of cobalt and nickel has been written by C. Krauss ("J.C.S.," 1891, A., p. 1139).

Uses and Storage.—Cobaltous nitrate is used in blowpipe analysis for the detection of alumina, zinc and magnesia, and, further, in the preparation of sodio-cobaltic nitrite, an important reagent for the precipitation of the heavy alkaline earths.

It precipitates rubidium salts from very dilute solutions, and detects the presence of potassium salts even when present in very small quantities. According to Hugo Erdmann ("Archiv. d. Pharm.," 1894, p. 22) the reagent may be prepared as follows: 30 gms. of crystallised cobaltous nitrate are dissolved in a mixture of 60 c.c. of water and 100 c.c. of concentrated solution of sodium nitrite (containing 50 gms.), and 10 c.c. glacial acetic acid added. When a few seconds have elapsed a copious evolution of nitric oxide will be observed, the cobalt being converted into the trivalent form, at once seen from the solution changing colour. As commercial sodium nitrite generally contains a trace of potash, a slight yellow precipitate generally separates out on standing, which must be filtered off. The reagent may also be prepared from the acetate according to the method given under "Sodium Nitrate" (see also above). Acetate of cobalt is also used for analytical purposes, and is tested in the same way as the nitrate. Cobalt salts must be kept in well-stoppered bottles.

Commercial Varieties.—The author has often found these to contain large quantities of the sulphate, and of nickel compounds.

COCHINEAL (INDICATOR AND PAPER).—See p. 74.

CONGO RED.—Congo red is the sodium salt of benzidin-disazo-bi-1-naphthylamine-4-sulphonic acid, and is formed by the action of tetrazo-diphenyl chloride on naphthionic acid. Red-brown powder soluble in water and alcohol, and the solution is very sensitive towards acids, a blue colour being produced; on addition of alkali the blue colour is changed to red. Congo red paper can be prepared by soaking paper in a solution of the dye; the blue paper is prepared by treating the red paper with acid. In literature on the subject several papers have appeared of late years on its value as an indicator, and among others one may refer to the contributions of Thomson, Vulpius, Julius, Williams, and Smith ("J.S.C.I.," 1886, p. 679; 1887, pp. 195, 739).

Congo red has been proposed as an indicator in the estimation of free acid, and in the titration of aniline, etc. Dieterich ("Pharm. Central.," 1887, p. 498) did not obtain good results

with congo red paper, on account of its lack of sensitiveness; on this subject see tables under "Indicators". Böckmann ("Chem.-techn. Untersuchungen," 3rd ed., vol. i., p. 139) also mentions the congo red colour as being one of those of less technical importance as an indicator. The test for proving the degree of sensitiveness of the indicator, is mentioned under "Indicators".

For full details on congo red, see Cohn, "Indicators and Test Papers," p. 65.

COPPER. — Cuprum metallic. puriss. (Cu). Mol. wt., 63·57. In the form of foil, wire, or a reddish powder.

Tests for Impurities.—*Iron, Silver, Lead, etc.*—2 gms. must dissolve in nitric acid to a clear solution, which must not turn turbid either with ammonia or hydrochloric acid; and on precipitating with hydrogen sulphide, filtering, evaporating to dryness and igniting, no weighable residue must remain.

Arsenic and Protoxide.—The arsenic is tested for by Marsh's test, but a simple method has been recommended by J. Clark ("J.S.C.I.," 1887, p. 352). The protoxide may be estimated by Hampe's method (see "Zeit. f. anal. Chem.," 1891, p. 344).

Appearance.—See under "Uses".

Quantitative Estimation.—The metal is dissolved in a sufficient quantity of nitric acid, the copper precipitated from the dilute solution with hydrogen sulphide, and the copper sulphide treated as under "Copper Oxide". For analyses of commercial samples of copper see Fresenius, "Quant. Anal.," vol. ii., p. 398 *et seq.*; also a paper by Murmann is detailed in "J.S.C.I.," 1897, p. 359.

Uses.—Pure metallic copper, obtained by precipitating with zinc in a copper sulphate solution, boiling with hydrochloric acid, and, if necessary, fusing under a layer of borax and rolling out into thin sheets, is employed for the precipitation of iron by Fuchs' method, and is also used for the detection of arsenic by Reinsch's method, the elaïdin test for oils and fats, and in the ultimate organic analysis of compounds containing nitrogen. For the latter purpose a good ordinary pure copper is sufficient. For analytical purposes copper is

used in the form of thin foil, wire, filings, turnings, and in the granulated state. Among other uses the turnings are employed to absorb any chlorine which may be evolved during the combustion of organic substances, in the analysis of iron and steel, and must therefore be perfectly pure, free from oil, and have a glistening appearance.

Commercial Varieties. — Even the purest specimens of metallurgical copper contain traces of impurities, particularly iron and protoxide of copper. Commercial precipitated copper, prepared as above, if not carefully and quickly dried, may assume a coating of verdigris which forms readily in a moist atmosphere. Further details see under "Uses". Copper wire and sheet are now prepared electrolytically in large quantities, and in a very pure condition.

Note.—On copper prepared by electrolysis, see Elbs, "Chem.-Ztg.," 1894, p. 1585.

COPPER AMMONIUM CHLORIDE.—Cuprum ammonium chloratum, puriss. ($2(NH_4Cl)CuCl_2, 2H_2O$). Mol. wt., 275·51. Blue crystals, giving a clear solution with water.

Tests for Impurities.—As under "Copper Sulphate". The salt must be absolutely free from sulphuric acid. Even after recrystallising several times, a slight acid reaction towards litmus remains. It is essential to recrystallise several times, and to prepare the salt only from the purest materials.

Uses.—In the estimation of carbon in iron, if a pure salt is not employed the results may be seriously vitiated. A. A. Blair ("J.S.C.I.," 1891, p. 574) believes that errors in carbon estimations are often caused by the presence of an organic substance in the salt. Copper-potasssium chloride ($2(KCl)CuCl_2, 2H_2O$) has been recommended in its place for effecting the solution of iron in the above estimations, and is prepared as follows: 107 parts ammonium chloride, 149·1 parts potassium chloride, and 170·3 parts crystallised copper chloride are dissolved in water, and the double salt crystallised out and purified by repeated crystallisation. Creath ("Chem. Centralblatt," 1877, p. 686) takes a solution containing 340 gms. copper chloride, and 214 gms. ammonium chloride in 1850 c.c. of water.

CUPRIC CHLORIDE. — Cuprum bichlorat. cryst. pur. ($CuCl_2, 2H_2O$). Mol. wt., 170·52. Green, deliquescent rhombic crystals, easily soluble in water and in alcohol.

Tests for Impurities.—As under "Copper Sulphate".

Sulphuric acid may be detected by barium chloride. The salt must dissolve completely in water or alcohol.

Arsenic.—1 gm. by Marsh's test (see "Zinc").

Quantitative Estimation.—See "Copper Sulphate, puriss."; the cuprous sulphide obtained, however, must be tested for lead.

Uses and Storage.—Berzelius employs a neutral solution of cupric chloride for the afore-mentioned estimation of carbon in iron, but now a solution of the chlorides of copper and ammonium is used, according to Creath ("Eng. and Min. Jour.," 23, p. 16). The salt must be carefully stored.

Commercial Varieties.—Copper chloride for technical purposes containing a large percentage of sulphate, and used as an oxidising agent, particularly in the preparation of methyl violet, can also be obtained. In testing such samples the percentage of copper present is the most important point; they must also give a fairly clear solution with water.

CUPRIC CHLORIDE, ANHYDROUS.—Pure dehydrated copper chloride is a brown powder, and on testing 1 gm. in Marsh's apparatus no arsenic reaction must appear. The salt must not contain any green hydrated particles, and must give an almost clear solution with water, i.e. only traces of oxide may be present. The salt must be carefully protected from moisture.

CUPROUS CHLORIDE.—Cuprum chlorat. alb. (monochlorat), (Cu_2Cl_2). Mol. wt., 198·06. A white powder, easily soluble in hydrochloric acid or ammonia. On exposure to atmosphere or light, absorbs water and oxygen, quickly turning green, forming the oxychloride.

Tests for Impurities.—The quality of the salt may be observed from its appearance, an imperfectly prepared sample having a green or brown colour. In testing the salt or estimating the copper present, it must first be oxidised and then

treated as under "Copper Sulphate". The presence of a small quantity of iron has no injurious effect for ordinary purposes. The solution in hydrochloric acid must readily absorb large quantities of carbonic oxide.

Uses and Storage.—Its solution in hydrochloric acid or ammonia is employed for the absorption of the gas just mentioned, and also some gaseous hydrocarbons; it can therefore be used for their quantitative estimation. In hydrochloric acid solution it may be used with advantage in the quantitative estimation of antimonietted and arseniuretted hydrogen (Riban, "Chem. Centralblatt," 1879, p. 348). Thomas ("Chem. News," 37, p. 6) describes there the preparation of a good cuprous chloride solution. In eudiometry the salt is employed in either hydrochloric or ammoniacal solution; the former solution is prepared by dissolving the salt in hydrochloric acid (1 : 124), and reducing the dark solution on the water bath by means of a copper spiral. The solution must be preserved under a layer of paraffin oil ("Chem.-Ztg.," 1891, p. 767).

Winkler prepares the ammoniacal solution by dissolving 250 gms. ammonium chloride in 750 c.c. of water, and, after transferring this solution to a well-stoppered bottle, adding 200 gms. of cuprous chloride. Ammonia is added when the solution is about to be used. Care must be taken to protect these solutions from the atmosphere, Hempel's gas pipette being generally employed for that purpose. The salt itself must be well protected from air and light.

Commercial Varieties.—These preparations are impure, and of a dirty green or brown colour.

COPPER OXIDE.—Cuprum oxydatum, pur. pulv. (CuO). Mol. wt., 79·57. Heavy, dense, deep black powder, gritty to the touch.

Tests for Impurities.—(*a*) On heating and passing moist air, free from CO_2, over 100 gms. of the sample, no fumes must be given off which redden blue litmus paper or produce a turbidity in lime water.

(*b*) 2 gms. are dissolved in hydrochloric acid and diluted to 100 c.c. with water; the solution must be almost clear. On precipitating with hydrogen sulphide, and evaporating the

filtrate to dryness and igniting, only a slight residue ought to remain (iron).

(*c*) The solution in hydrochloric acid must not show a turbidity with either barium chloride or sulphuric acid.

(*d*) 20 gms. are extracted with cold, very dilute nitric acid, and the copper dissolved precipitated with hydrogen sulphide, and the filtrate evaporated to dryness and ignited; only a slight residue must remain (iron). The residue is also tested for alkalies and alkaline earths, particularly lime, which is detected by dissolving the residue in dilute acid, adding excess of ammonia, filtering, and adding ammonium oxalate to the filtrate; if any precipitate appears it is ignited and weighed as CaO.

Note.—Fresenius, in his book on "Quantitative Analysis," remarks on the presence of lime, particularly where the oxide has been prepared from copper scales, and for its elimination he treats the oxide with dilute nitric acid, and proceeds according to (*d*). Nencki (see also under "Lead Chromate") has tested samples obtained from various manufacturers, but found only a few free from that impurity. One sample contained as much as 1·02 per cent. CaO. He also remarks that lime may be detected by a method described in a former (German) edition of this book, but we consider its presence may easily be overlooked by that test. He emphasises the fact that his attention was first called to the presence of lime in commercial copper oxide by his friend, Mr. Kostanecki; he, therefore, was as much in the dark as the present author, who was also first made aware of its presence by Kostanecki's discovery. As a result, this special test for lime has been added.

Quantitative Estimation.—The above tests provide a sufficient guarantee of purity, but if a quantitative estimation is required the oxide may be dissolved in excess of hydrochloric acid, the solution filtered, and the copper precipitated in the hot filtrate with hydrogen sulphide. The sulphide is then reduced in a current of hydrogen to the protosulphide and weighed as such. The sulphide must be tested for lead. Fresenius ("Quant. Anal.," vol. i., pp. 257, 456, 463) mentions precautions to be observed in employing this method, and also the complete separation of copper from other metals.

Uses and Storage.—The oxide is used in ultimate organic analysis, and on this account must be well protected from

dust. According to Frankland and Armstrong, copper oxide prepared from the nitrate contains slight traces of nitrogen and carbon dioxide. Copper oxide in the form of wire is therefore said to be better for nitrogen estimations than the granulated or powdered form (see Richards, "Chem. News," vol. lxvi., p. 74).

Commercial Varieties.—Pure granulated copper oxide for ultimate organic analysis can also be obtained, and is tested as given above. On solution in hydrochloric acid this form always leaves a distinct residue, an occurrence which cannot be avoided as the oxide is prepared by strong ignition in a Hessian crucible. The pure oxide can also be procured in the form of wire, also for use in ultimate organic analysis. Other varieties are copper oxide, for technical purposes, and copper hydrate; the latter is used in the quantitative estimation of albuminoids for which purpose it is specially prepared by precipitation from copper sulphate with caustic soda, and is kept moist by adding a little glycerine. For a detailed description of its preparation, estimation, and storage, see Allen's "Comm. Organ. Anal.," vol. iv., p. 30.

CUPRAMMONIUM HYDROXIDE (Schweitzer's Reagent).—This solution is formed on shaking together metallic copper and ammonia in presence of air, and is used as a solvent for cellulose, which it converts into oxycellulose. A good method of preparing the solution is as follows: A quantity of copper sulphate is precipitated with ammonia till a slight darkening of the solution indicates excess of ammonia, the precipitate is washed several times by decantation, then digested for some time in the cold with water and caustic soda solution, again washed and the precipitate finally dissolved in very strong ammonia.

COPPER SULPHATE.—Cuprum sulphuric. puriss. cryst.: sulphate of copper ($CuSO_4$, $5H_2O$). Mol. wt., 249·71. Beautiful blue trilicnic crystals, giving a clear solution with water (1 : 3).

Tests for Impurities.—On dissolving 3 gms. in about 80 c.c. of water, and precipitating the copper with hydrogen sulphide,

the filtrate, when evaporated to dryness and ignited, must leave only traces of residue.

Iron.—5 gms. are dissolved in 25 c.c. of water and 15 c.c. of ammonia added, which redissolves the precipitate at first formed; the solution is then filtered through a 10 c.m. filter paper, and washed alternately with water and ammonia until the paper ceases to be blue; no brown spots must remain; these are particularly apparent on drying the paper (Ronde).

Quantitative Estimation.—The copper sulphate is dissolved in water, hydrochloric acid added, and the copper precipitated with hydrogen sulphide in the warm solution. The precipitate is then converted into the protosulphide by igniting in a current of hydrogen, and weighed as such (see "Copper Oxide").

Uses.—The pure salt is used in the preparation of Fehling's solution for sugar estimation (see p. 108), also in the solutions of Löwe and Worm-Müller, for the same estimation. A mixture of copper sulphate and ferrous sulphate precipitates copper iodide from the neutral solutions of the metallic iodides. Copper sulphate alone, containing SO_2, precipitates iodine in combination, and is employed in analysis for that purpose. A solution of the salt with ammonia in excess is used as a test for carbon disulphide. For the detection of free and combined acid in solutions of the heavy metals a solution of the salt with slight excess of ammonia added is employed under the name of Kieffer's reagent.

Commercial Varieties.—The salt is generally fairly pure; the presence of a large quantity of iron may be recognised by the greenish colour of the crystals; traces of the sulphates of zinc, lime, and magnesia are sometimes detected.

COPPER SULPHATE, ANHYDROUS.—The salt is used for the detection of moisture, e.g. in testing ether, and may be prepared by drying the pure copper sulphate at 200° C. in an air bath till only a white powder remains: it is also used in the estimation of boracic acid by Morse and Burton's method; it has also been suggested for the estimation of fat in milk (Morse and Piggott, "J.C.S.," 1887, A., p. 752). Tests for purity as under preceding preparation. On heating to about

150° C. no water must be given off; traces of iron need not be objected to.

CUPFERRON.—Colourless or yellowish crystals. M.p., 163°-164°. Ammonium salt of nitrosophenylhydroxylamine ($C_6H_5 . N . [NO] . O . NH_4$). This was discovered by O. Baudisch in 1909 to be capable of precipitating iron and copper quantitatively, and to be extremely useful for separating these metals from several others.

Iron is completely precipitated in the cold from solutions containing hydrochloric, sulphuric, or acetic acid in the form of reddish-brown flocks, the compound having the formula $(C_6H_5 . N . [NO] . O)_3 Fe$, the separation from Cr, Al, and other metals being complete. Copper may also be precipitated in greyish-white flocks, and thus can be separated from Cd, Zn, and several other metals. (A. Chaston Chapman, "Proc. Chem. Soc.," 1917, p. 214). When copper and iron exist together in solution, they are both precipitated; but the copper compound may be separated by treatment with ammonia in which it is easily soluble (see also O. Baudisch, "Chem. Zeit.," 1909, p. 1298; Merck's "Annual," 1909, p. 174; 1911, p. 152).

Titanium is completely precipitated by cuproferron in tartaric acid solution, and may in this way be separated from iron (W. M. Thornton, jun., "Amer. J. Sci.," 1914, 37, pp. 173-178; "J.S.C.I.," 1914, p. 279). Thorium is also precipitated similarly (*ibid.*, "Chem. News," 1916, 114, pp. 13-14). A very important paper on the quantitative separations with cupferron is by O. Baudisch ("Chem. Zeit.," 1909, pp. 1298-1300; "J.S.C.I.," 1910, p. 115).

DIAZOBENZENE SULPHONIC ACID.—If a small quantity of an alcohol or substance containing an alcoholic hydroxyl group is heated with diazobenzene sulphonic acid (or sulphanilic acid and sodium nitrite) and sodium or potassium hydroxide, a red or brown colour is developed. This serves for the detection of all alcohols, glycerol, etc., it may also be employed for detecting malic acid in presence of tartaric and citric acids (L. Rosenthaler, "Chem. Zeit.," 1912, 36, p. 830; "J.S.C.I.," 1912, p. 741).

DICYANDIAMIDINE SULPHATE.—May be employed for the detection of nickel in presence of cobalt. To the solution to be tested 10 to 20 c.c. of a 10 per cent. solution of sucrose is added, then a solution of dicyandiamidine sulphate and sodium hydroxide. In presence of nickel a well-crystallised precipitate of nickel dicyandiamidine quickly separates, while the liquid changes to deep red or reddish-violet if cobalt is also present, this is characteristic (H. Grossman and W. Heilborn, "Ber.," 1908, 41, pp. 1878-1880).

DIGITONIN. — Digitalin. Is a digitalis glucoside, $C_{27}H_{46}O_{14} + 5H_2O$. Softens at 225° and melts at 235°. Slightly soluble in water, solution froths on agitation, insoluble in ether and chloroform, but sparingly soluble in alcohol. It was discovered by Windhaus in 1910 that digitonin gave a crystalline precipitate with cholesterin—

$$C_{27}H_{46}O + C_{55}H_{94}O_{28} = C_{82}H_{140}O_{29}.$$

It also yields a precipitate with phytosterin, and is now employed for separating these alcohols from animal and vegetable fats and incidentally for distinguishing the two classes since the alcohols can be recovered from the digitonides and recognised by their crystalline forms and the melting points of their acetates ("Zeit. fur physiol. Chem.," 1910, 65, p. 110; Merck's "Annual," 1910, p. 162).

DIMETHYLAMIDOBENZALDEHYDE. — Paradimethylamidobenzaldehyde $(CH_3)_2N.C_6H_4.CHO$. Yellow crystals soluble in water and alcohol. M.p., 73°.

Uses.—A solution containing 0·33 gm. in 50 c.c. of strong hydrochloric acid and an equal volume of water is used as a test for indican in urine (Ehrlich's Test). On boiling with this reagent, cooling, and adding ammonia a red colour develops.

Note.—Jaffe's test for indican consists in adding an equal volume of strong hydrochloric acid and a solution of bleaching powder drop by drop; if indican is present a blue colour due to indigo is produced.

DIMETHYL ANILINE.—Formula $C_6H_5N(CH_3)_2$. Mol. wt., 121·14. Yellowish or brownish oily liquid. Sp. gr., 0·961.

B.p., 193°. Slightly soluble in water, mixes with alcohol and ether in all proportions.

Uses.—Dimethylaniline is employed as a test for nitrites (E. H. Miller, "Analyst," 1912, 37, p. 345; Merck's "Annual," 1912, p. 169).

DIMETHYLGLYOXIME, $CH_3C(NOH)C(NOH)CH_3$. — Mol. wt., 116·10. White crystals. M.p., 240°.

Dimethylglyoxime forms a delicate test for nickel, with which it gives a red colour. The reaction was discovered by Tschugaev in 1905, who found that 1 part of nickel could be detected in more than 1,000,000 parts of water, and that even when cobalt was present to the extent of 5,000 times that of the nickel the latter could with certainty be detected. The reaction is shown as follows :—

$$2C_4H_8O_2N_2 + NiCl_2 + 2NH_3 = (C_4H_7O_2N_2)_2Ni + 2NH_4Cl.$$

This reagent can be employed in estimating nickel in presence of cobalt, zinc, and iron. It is also used in detecting nickel in hydrogenated fats. For this purpose 10 c.c. of the fat is heated with 2 c.c. of strong HCl; the acid liquid is separated and evaporated nearly to dryness; excess of ammonia is then added and a few drops of dimethylglyoxime solution. When in presence of nickel a rose-red colour is produced.

Note.—a-benzildioxime, also discovered by Tschugaev, has been suggested by Atack also for detecting and estimating nickel with which it forms an even more intense red compound ($C_{28}H_{22}O_4N_4Ni$). It is stated to be capable of detecting 1 part of nickel in 10 million parts of water (A. Chaston Chapman, "Proc. Chem. Soc.," 1917, p. 213; Merck's "Annual," 1910, p. 165; 1912, p. 170).

Dimethylglyoxime can also be used as a delicate test for ferrous salts (P. Slawik, "Chem. Zeit.," 1912, p. 54; "J.S.C.I.," 1912, p. 126). Ferrous salts yield with 1·2-dioximes an intense red colour, thus with dimethylglyoxime the reaction is so extremely sensitive that 0·0000007 Fe″ can be detected. Ferric salts do not give the reaction. This reagent may therefore be used for determining iron in presence of Zn or Al; alkalies and alkaline earths do not affect it (L. Tschugaeff and B. Orelkin, "Z. anorg. Chem.," 1914, 89, pp. 401-404; "J.S.C.I.," 1915, p. 101).

Dimethylglyoxime is used for the quantitative precipitation of nickel, it also precipitates palladium quantitatively but not tin (A. Gutbier and C. Fellner, "Z. anal. Chem.," 1915, 45, pp. 205-208).

DIMETHYLPARAPHENYLENEDIAMINE HYDROCHLORIDE.—Formula $C_6H_4NH_2N(CH_3)_2$ 2HCl. White or greyish-white hygroscopic crystalline powder. Slightly soluble in water.

Uses.—Is employed in the detection of ozone, hydrogen peroxide, and uric acid, also in the detection of olive stones in pepper (Merck's "Index," pp. 96, 281).

DIMETHYLSULPHATE, $SO_2(OCH_3)_2$.—Sp. gr., 1·334. B.p., 188° C. Colourless liquid, very soluble in alcohol and in ether, insoluble in water.

Uses.—As shown by Valenta ("Chem. Zeit.," 1906, p. 266) this is a useful reagent for the examination of mixtures of coal-tar oils and petroleum hydrocarbons, the former being soluble and the latter insoluble (see also Lewkowitsch, "Chemical Technology of Oils, Fats, etc.," 5th ed., vol. i., p. 611).

DIPHENYLAMINE.—Diphenylamin pur. $((C_6H_5)_2NH)$. Mol. wt., 169·15. White crystals. M.p., 53°. B.p., 300°. Insoluble in water, easily soluble in alcohol and ether.

Tests for Impurities.—0·2 gm. diphenylamine must give a colourless solution with (1) 2 c.c. pure dilute (1 : 5) sulphuric acid, and (2) 20 c.c. concentrated.

Quantitative Estimation.—The melting point and behaviour towards sulphuric acid are guides as to the purity of the diphenylamine.

Uses.—Diphenylamine Solution, and Application of the Diphenylamine Reaction.—The reagent is prepared by dissolving 0·5 gm. diphenylamine in 100 c.c. pure concentrated sulphuric acid, with the addition of 20 c.c. of water. In testing for acids of nitrogen, a few c.c. of the specifically heavier liquid are first poured into a test tube or beaker (sulphuric acid of 66° would be poured in first, but in the case of a lighter gravity, the diphenylamine solution would occupy the lower layer); over this is then poured a layer of the specifically lighter liquid, and a few minutes are allowed to elapse for the purpose of observing whether a cornflower blue ring forms at the juncture. For better observation the glass is held in a slanting position against a white background (Lunge, "Zeit. f. angew. Chem.," 1894, p. 345; abst. "J.S.C.I.," 1895, p. 67). Lunge states that the method adopted by A. Wagner is not so accurate, and the author

has also repeatedly made the same observation.[1] Regarding the use of diphenylamine in testing milk for nitric acid by Soxhlet's method, see "J.S.C.I.," 1886, pp. 546, 618. In carrying out the diphenylamine test a sulphuric acid free from nitrogen is necessary; the acid must be tested previously on diphenylamine, as described above, and must not show the slightest blue colour. The pure sulphuric acid from the various factories, and particularly the pure acid for analysis, manufactured by Messrs. E. Merck, fulfils these conditions. Some time ago it was a difficult matter to obtain pure sulphuric acid perfectly free from nitrogen in the market. It is employed for detecting wood pulp in paper. Diphenylamine has been also suggested as a test for laevulose in urine (Jolles, "Apotheker Zeitung," 1909, p. 719).

Commercial Varieties.—Commercial diphenylamine is often impure and dissolves in sulphuric acid with a strong yellow colour.

1·2-DIAMINOANTHRAQUINONE-3-SULPHONIC ACID.—According to R. Uhlenhuth ("Chem. Zeit.," 1910, 34, p. 887) 1·2-diaminoanthraquinone-3-sulphonic acid forms a very delicate test for salts of copper with which it yields a deep blue coloration. The reagent is prepared by dissolving 0·5 gram of the substance in 500 c.c. of water and adding 40 c.c. of sodium hydrate solution of 40° B. With this solution 0·0000019 gram of Cu in 1 c.c. can readily be detected.

DIPHENYLBENZIDINE.—According to Wieland ("Ber.," 1913, 46, p. 3296) in the diphenylamine reaction for nitrites and other oxidising agents, diphenylbenzidine is first formed. This was confirmed by H. Muraour ("Bull. Soc. Chim.," 1914, 15, pp. 186-187; "J.S.C.I.," 1914, p. 335), who recommends the use of this reagent as being a more sensitive reagent for nitrites, and gives a method for its preparation.

DIPHENYLCARBAZIDE.—Was used by Cazeneuve for detecting the metals copper and mercury and also CrO_3, with which it formed characteristic coloured compounds ("Compt. Rend.," 131, p. 346; "J.S.C.I.," 1900, pp. 1007, 1040); also employed by R. Oddo as an indicator in the volumetric estimation of mercurous compounds ("Gaz. Chim. It.," 1909, i., p. 666;

[1] Wagner's method is described in the second (German) edition of this book.

"J.S.C.I.," 1909, p. 913), with which it gives an intense blue coloration.

On the use of diphenylcarbazide as an indicator in the titration of iron with bichromate, see O. L. Barneby and S. R. Wilson, "J. Amer. Chem. Soc.," 1913, 35, pp. 156-162; "J.S.C.I.," 1913, p. 254.

ETHER, ETHYL.—Æther puriss. ($C_4H_{10}O$). Mol. wt., 74·28. Clear, colourless, very mobile liquid, showing a neutral reaction. B.p., 34·9°. Sp. gr., 0·720. Slightly soluble in water (1 : 12), mixes with alcohol in all proportions.

Note.—An ether which at first shows a specific gravity of 0·720 may rise to 0·721 after having been decanted several times. This can be explained in the following way: During the pouring out, water is condensed in contiguity to, and on the surface of the flowing ether, owing to the cold produced by evaporation, and this increases the specific gravity. For experiments on this point, see "Pharm. Ztg.," 1892, p. 56.

Tests for Impurities.—*Odour* (heavy oil of wine and fusel oil).—Filter paper which has been moistened with ether must not retain any smell on evaporation of the latter.

Note.—In the "Zeit. f. anal. Chem.," 1886, a case of adulteration of ether with petroleum spirit is mentioned.

Residue.—On spontaneous evaporation of 20 c.c. of ether in a glass dish the moist residue must have no smell, and must neither redden nor bleach blue litmus paper. The moist residue must evaporate completely on the water bath.

Acidity.—On shaking about 10 c.c. of ether with 3 c.c. of water, the latter must show no acid reaction.

Note.—According to Vulpius ("J.S.C.I.," 1887, p. 750), the reaction with phenolphthalein is very delicate. In the case of three kinds of ether, on shaking 20 c.c. of each sample with 10 c.c. of water and 2 drops of phenolphthalein solution, the first used 0·1, the second 0·2, and the third 5·2 c.c. more $\frac{n}{100}$ alkali, to produce the same depth of colour than a test using water alone. The first two were good samples, and the last bad. In testing for acid, therefore, this method must always be used. I may add that, according to observations made in Schering's Laboratory, even the purest ether gave a blue reaction with moist red litmus paper ("Pharm. Central.," 1895, p. 41). The author has often had to complain of ether which contained sulphuric acid. Water, on being shaken with such ether, not

only showed a strong acid reaction, but also gave a heavy precipitate with barium chloride.

Hydrogen, Peroxide, Ozone, and Aldehyde.—(*a*) 10 c.c. of ether and 1 c.c. of potassium iodide solution, when frequently shaken in a well-stoppered bottle, must show no coloration during one hour's exposure to diffused daylight.

(*b*) 30 c.c. of ether and about 5 gms. of solid potash, after standing for one day in a dark place and being occasionally shaken, must show no appearance of a brownish substance having separated out.

Note.—Concerning the above tests, it must be added that the test with potash may show, besides aldehyde, the presence of vinyl alcohol. The presence of aldehyde can be detected by fuchsine-sulphurous acid ("J.S.C.I.," 1894, p. 1098). The best test for aldehyde (and alcohol) is Nessler's reagent, but it is not possible to obtain an ether which does not respond to this test (Lassar-Cohn, "Rep. d. Chem.-Ztg.," 1895, p. 58; Liebig's "Ann. Chem.," 1895, 284, p. 266; and "J.S.C.I.," 1895, p. 295). Hydrogen peroxide is also easily detected by adding potassium iodide and starch solution, iodine being liberated, and giving a blue coloration. Another good method is based on the fact that hydrogen peroxide oxidises chromic acid to perchromic acid, which dissolving in ether gives a blue colour. Some potassium chromate, with a few drops of dilute sulphuric acid, is added to the ether, and the mixture well shaken; a blue colour shows presence of hydrogen peroxide. The presence of vinyl alcohol can be detected, according to W. Bertsch ("Apoth. und Drogist," 1893, No. 12), by shaking the ether with mercury oxychloride. If, after 10 or 20 minutes, a turbidity or a white amorphous precipitate appears (vinyl mercury oxychloride), which, on treatment with potash, is converted into a black explosive powder, the presence of vinyl alcohol may be safely assumed. On the formation of the impurities just mentioned during storage, see note under "Uses". A detailed account by Arends of the more recent works on the properties, testing, and purification of ether can be found in the "Pharm. Ztg.," 1896, p. 663.

Sulphur Compounds.—About 10 c.c. of ether are shaken in a small glass bottle with 1 drop of pure mercury, after which the mercury must retain a clean surface and no black powder must be formed.

Note.—The above test has been suggested by Professor L. Koninck. According to the "Pharm. Ztg.," 1889, p. 222 ("J.S.C.I.," 1889, p. 215), the black colour appears not only in presence of sulphur, but also if hydrogen peroxide is present.

Water.—Dehydrated sulphate of copper must not turn green or blue on shaking with ether.

Note.—On testing for water, see also note under "Ether Puriss. Distilled Over Sodium". Ether used for the estimation of fats ought to be as free as possible from water.

Alcohol.—The most delicate test for alcohol and water is undoubtedly the coloration produced by adding crystals of acetate of rosaniline, previously dried at 100°. The iodoform test is very delicate so far as the presence of alcohol is concerned, but as a rule the estimation of the specific gravity is sufficient (see under "Quantitative Estimation"). Alcohol and water may also be tested for by shaking 10 c.c. of the ether with water previously saturated with ether; there should be no diminution of volume in the upper layer of liquid.

Quantitative Estimation.—Estimation of the boiling point, and especially of the specific gravity, combined with the tests mentioned above, are sufficient to determine the purity of an ether.

Commercial ethers, containing considerable quantities of water and alcohol, show a high specific gravity, and immediately colour dehydrated copper sulphate blue. If the boiling point of an ether has to be estimated this must only be done on the water bath, and never over a naked flame, especially as ether containing small quantities of hydrogen peroxide or ethyl peroxide gives rise to violent explosions at the end of the distillation. For this reason also the ether should be redistilled before using for fat, etc., extractions, otherwise the flask will be shattered. For a table of the specific gravities of mixtures of ether and alcohol, see Squibb, "J.S.C.I.," 1884, p. 531.

Hager (see Hager's "Handbuch der Pharm. Praxis," Berlin, 1876, vol. i., p. 167; also Allen's "Comm. Organ. Anal.," vol. i., p. 180) estimates approximately the quantity of alcohol in ether by observing the degree to which the ether dissolves in water, or the alcohol may be determined by Lieben's method, which consists in shaking the ether with water, and heating the water with iodine and potash (formation of iodoform).

The ether is often qualitatively tested for alcohol by shaking it with the same volume of water. A good ether

must not dissolve in water to the extent of more than 10 per cent. The test is superfluous if the ether shows the correct specific gravity. If the correct temperature is not maintained erroneous results may be arrived at on shaking with water. It may be assumed that ether of 0·720 sp. gr. ("Pharm. Germ.") contains 0·1 per cent. of water and 0·8 per cent. of ethyl alcohol. An analysis of an ether of 0·724 sp. gr. ("Pharm. Centralhalle," 1894, p. 118) showed 95·9 per cent. absolute ether, 3·72 per cent. absolute alcohol, and 0·38 per cent. of water; that is, roughly speaking, 96 per cent. ether and 4 per cent. alcohol of 90 per cent. According to Squibb (loc. cit.) an ether of 0·720 sp. gr. contains about 1 per cent. of alcohol.

Uses and Storage.—Ether as a solvent plays an important part in the estimation of fats (for the quality of ether required for such purposes, see previous remarks). It is used further for the extraction of alkaloids and for various separations in inorganic analysis.

In working with ether there must be no naked flame near it; it must only be distilled on a water bath, which obtains its heat indirectly. As during storage a number of decompositions can take place (see note below), certain precautions are necessary. It is best stored in small, well-stoppered, brown bottles of such capacity that they need not often be opened before being emptied, and these bottles should be kept in a dark, dry place.

Note.—Ether (no doubt during storage) forms such oxidation products as acetaldehyde, hydrogen peroxide, ethyl peroxide, acetic acid, and vinyl compounds (see Thoms, "Pharm. Ztg.," 1894, 777, and "Ber. d. Pharm. Ges.," Berlin, 1894, parts 10 and 11).

These products are formed through contact with air in presence of light, as well as in the dark. According to Berthelot, perfectly pure ether can form on long standing under the influence of air, traces of ethyl peroxide, or of nitric acid.

A. Richardson ("J.C.S.," 1891, A., i., pp. 51-58) has proved further that pure ether forms hydrogen peroxide by the action of sunlight in presence of moist oxygen. Dunstan and Dymond obtained the same result.

Richardson found that hydrogen peroxide is formed when pure ether and moist oxygen are subjected in closed vessels to a temperature of from 60° to 88° in the dark for several days. Many observations prove that the formation of hydrogen peroxide in ether is

not due to impurities ("Pharm. Ztg.," 1892, p. 45; "J.S.C.I.," 1892, p. 835). The liquid evaporates very quickly in badly-stoppered bottles, and often forms considerable quantities of the above impurity. Ether containing the aforementioned compounds has been known to cause very dangerous explosions (for particular reference to this point, see Schär, "Arch. d. Pharm.," 1887, p. 623 *et seq.*; "J.S.C.I.," 1887, p. 680). The author of this book found a strong acid reaction in an ether which caused an explosion during an estimation of fat. This ether was the last of a supply which had been in use for three months and had been kept in a corked bottle. It was originally a pure neutral sample.

P. H. Cleve ("J.C.S.," 1891, p. 15) describes a peculiar explosion due to impurities. After distilling about 250 c.c., a tough residue remained which, when dried on the water bath, formed a transparent amorphous mass, weighing about 0·75 gm. After Cleve had added a little water and was stirring carefully with a rounded glass rod, a violent explosion occurred.

The explosive substance was evidently ethyl peroxide, as it showed the well-known perchromic coloration; it also liberated iodine and formed oxygen with oxide of silver. Reducing agents decomposed it spontaneously, and it exploded as violently as chloride of nitrogen.

I might further mention suggestions which have been made for the purification of ether which has deteriorated. Ether may be purified from hydrogen peroxide by shaking with manganese dioxide (see "Rep. d. Chem.-Ztg.," 1889, p. 46). On its purification by means of caustic potash, see Allen's "Comm. Organ. Anal.," vol. i., footnote, p. 177. Ether which is not perfectly free from acid must be treated with solid caustic potash before use (see "Estimation of Free Acid in the Contents of the Stomach," "Arch. d. Pharm.," 1888, p. 34). On the existence of vinyl alcohol in ether, see Poleck and Thümmel ("J.C.S.," 1890, A., p. 118).

Hydrogen peroxide may also be eliminated by shaking with permanganate of potash, or by treating the ether with chromic acid. An ether perfectly free from aldehyde is obtained, according to Crismer, by precipitating the aldehyde with Nessler's reagent, separating the liquids by means of a separating funnel, drying with potassium carbonate and redistilling.

According to M. Ekenberg ("J.S.C.I.," 1894, p. 62), an ether sufficiently pure for laboratory purposes is obtained on mixing ordinary ether, containing water, alcohol, and oxidation products, with 5 to 10 per cent. by volume of liquid paraffin, and afterwards distilling at from 40° to 50°.

Commercial Varieties.—The different varieties are generally given in the catalogues with a certain guaranteed specific gravity. For analytical purposes undoubtedly only the pure

ether described above and the quality distilled over sodium should be used. Formerly inferior ether of 0·730, and even higher specific gravity, was frequently used for the estimation of fats. On the composition of commercial varieties, see under "Quantitative Estimation".

ETHER, ETHYL, FREE FROM WATER, DISTILLED OVER SODIUM.—Æther puriss. Free from water, distilled over sodium ($C_4H_{10}O$). Mol. wt., 74·28. Sp. gr., 0·718-0·720. B.p., 34·9°.

Tests for Impurities.—The tests are conducted as under "Æther puriss. 0·720 sp. gr.". Water shaken with the ether must show neither acid nor alkaline reaction.

Test for Water.—15 c.c. of the ether are put into a perfectly dry test tube and a piece of pure metallic sodium, about the size of a pea, is added. Only a very slight evolution of gas should take place, and the sodium must show, even after standing for 6 hours, a distinct metallic lustre.

In a sample not previously treated with sodium the metal, during the test, becomes surrounded with a yellowish-white coating of sodium hydrate.

Note.—In the literature on this subject the following tests for the examination of ether for water are suggested :—

(*a*) Mixing with an equal part of carbon disulphide must produce no turbidity (Beilstein, "Organische Chemie").

(*b*) On shaking with dry tannin (perfectly dry or air-dry?—author's query) the latter must not liquefy, but remain in the form of a powder (Hager).

(*c*) Paper coloured blue with cobalt trichloride must not change colour (Napier).

The author has tried further :—

(*d*) A test with dehydrated copper sulphate, which, as is well known, turns green or blue in presence of water. He has tested various ethers according to methods (*a*), (*b*), and (*d*), and the above test with sodium with the following results :—

1. Ether, sp. gr. 0·725, stood none of the tests.
2. Ether puriss., sp. gr. 0·720-0·722, stood all tests except the one with sodium.
3. Ether, distilled over sodium, stood all tests.

The ether puriss. of sp. gr. 0·720, is, therefore, as it stands, fairly good as regards freedom from water, and is perfectly adapted for most analytical purposes. The product distilled over sodium

contains even less water and alcohol. The last mentioned as well as the ether puriss., sp. gr. 0·720, must be kept in the dark.

Quantitative Estimation.—See under "Æther Puriss.," p. 102.

Uses.—Among other uses, the purest ether is employed in the estimation of alkaloids. For that purpose it must be perfectly free from alcohol and heavy oil of wine (see further under "Æther Puriss." in the foregoing article).

Commercial Varieties.—See under "Æther Puriss.," p. 104.

ETHER, PETROLEUM.—Benzin petrolei (æther petrolei). The colourless, nonfluorescent portions of petroleum which distil over almost completely between 40° and 75°. Sp. gr., 0·64 to 0·68.

Tests for Impurities.—*Odour.*—The smell must neither resemble tar (coal-tar naphtha) nor mustard (lignite benzine). The smell must be an agreeable one, and not strong.

Five drops treated with 40 drops of strong sulphuric acid and 10 drops of nitric acid, should on dilution yield no odour of bitter almonds (absence of benzene).

Boiling Point.—See above.

Note.—In estimating the boiling points of samples it must be borne in mind that each single fraction contains also considerable quantities of lower and higher boiling points, that is to say, the oils boil within considerable limits of temperature, as the temperatures at which they have been condensed indicate (see "Post, Chem.-techn. Analyse," vol. i., p. 308).

Quantitative Estimation.—The quantitative estimation is performed by determining the boiling points.

Uses and Storage.—Petroleum ether is used as a solvent for alkaloids and many other substances. On petroleum ether for forensic purposes, see under "Benzene". As the compound is highly inflammable, it is necessary to use the greatest precautions, both in the use and storage of it.

Commercial Varieties.—The commercial varieties, which vary considerably in their boiling points, are exhaustively described in Hager's "Commentar zur Pharm. Germ.," ii., p. 448 *et seq.* According to Hager, wood spirit is used for adulterating, or acting as a substitute for, petroleum ether.

The likelihood of the so-called coal-tar naphtha being present may also have to be considered. Hager describes

a test consisting of dropping the ether on to a piece of glass. On testing the commercial varieties, see Hager's "Handbuch d. Pharm. Praxis."

According to F. Evers ("J.S.C.I.," 1891, p. 753) petroleum ethers are met with in commerce boiling between 32° and 110°, and having a decided smell of bitter almonds on testing with nitro-sulphuric acid (benzol). This test is given by the German Pharmacopœia. On distilling 100 c.c. of this so-called petroleum ether, the following results were obtained:—

Temp.	Quantity Obtained on Distillation.
32°	1 drop
33°	5 c.c.
36°	10 c.c.
40°	20 c.c.
43°	30 c.c.
47°	40 c.c.
51°	50 c.c.
57°	60 c.c.
65°	70 c.c.
78°	80 c.c.
94°	90 c.c.
105°	95 c.c.
110°	98 c.c.

Taking into consideration the irregularity of the boiling points, and the evidence of benzene being present, Evers concluded that the petroleum ether in question had been adulterated with "hydro-carbon," or with waste products from the manufacture of benzene from hydrocarbon. The latter is now obtained in large quantities as a by-product from railway companies' gasworks, and it can be so far purified that it has the appearance of a colourless distillate with an odour of benzene. It contains up to 50 per cent. of benzol and toluol and hydrocarbons of the ethylene series.

It is necessary to remark, with reference to these experiments of Evers, that, according to Engler, all crude petroleum, whether Russian or American, contains aromatic hydrocarbons, such as benzol, toluol, and xylol. In the preparation of

petroleum ether the low boiling portions of the crude petroleum are treated with sulphuric acid to eliminate benzol, etc. Should the aforesaid treatment be somewhat imperfect, even an unadulterated petroleum ether may contain a small quantity of benzol; it then has a smell of oil of bitter almonds on applying the nitro-benzene test of the Pharm. Germ. According to L. Reuter and others, even well-known dealers in chemicals were unable to supply petroleum ether which stood the said nitro-benzol test ("Pharm. Ztg.," 1891, p. 270). The author has therefore purposely omitted that test.

ETHYL ORANGE.—Sodium salt of p-Diethylamidoazo-benzol sulphonic acid. Gives with alkalies a yellow colour and with acids red. Very similar to methyl orange but less sensitive (see indicators).

EUGENOL.—Eugenic or caryophilic acid ($C_{10}H_{12}O_2$). $C_3H_5 . C_6H_3(OCH_3) . OH$. Mol. wt., 164·15. Sp. gr. at 15°, 1·072 to 1·074. Slightly soluble in water, easily soluble in alcohol and ether (see Fourth Germ. Pharmacopœia).

This substance and also the oil of cloves from which it is extracted find a use in microscopy. It is an aromatic liquid, and, according to Schimmel, pure eugenol should give a clear solution in 1 to 2 per cent. caustic potash solution, have a sp. gr. as above at 15°, and a boiling point from 253°-254° (mercury column wholly immersed in the vapour), (247°-248° Merck). The valuation of oil of cloves is based on the percentage of eugenol it contains. The latter is separated as benzoyl-eugenol, according to H. Thoms, and the method is described, *inter alia*, in "J.S.C.I.," 1893, p. 184; see also Erdmann ("J S.C.I.," 1897, p. 1050), who found 82·80 per cent. of eugenol in oil of cloves. The estimation is also carried out by determining the amount soluble in caustic potash solution. See Allen's "Organic Analysis," 3rd ed., vol. ii., pt. iii., p. 361.

FEHLING'S SOLUTION.—Also potassio cupric carbonate solutions. Fehling's solution is prepared as follows: The purest copper sulphate is powdered slightly and exposed to the atmosphere for 12 hours, all dust being carefully excluded;

34·63 gms. are now dissolved in 500 c.c. of water. The alkaline tartrate solution should be freshly prepared as often as possible, and is formed by dissolving 173 gms. Rochelle salts in 400 c.c. of water and adding 100 c.c. of caustic soda solution containing 516 gms. per litre. Fehling's solution consists of equal proportions of these two solutions, and they should only be mixed for immediate use. Each c.c. of Fehling's solution = 0·005 gm. of glucose.

Note.—Soldaini recommends, for sugar estimation, potassiocupric carbonate solution in place of the above, and, according to Ost, this solution may be easily prepared by dissolving 23·5 gms. copper sulphate, 250 gms. potassium carbonate, and 100 gms. potassium bicarbonate in water, and making up to 1 litre ("J.C.S.," 1890, A., p. 198). A detailed account of these copper solutions is given in "Chem. Ztg.," 1895, Nos. 80 and 81.

Note.—A modification of Fehling's method which may with advantage be employed has been devised by Gerrard ("Year Book of Pharm.," 1892, p. 400). This depends on the fact that a solution of a copper salt is decolorised by potassium cyanide, the double cyanide of copper and potassium being formed :—

$$CuSO_4 + 4KCN = Cu(CN)_2 . 2KCN + K_2SO_4.$$

The method is as follows: 10 c.c. of the mixed Fehling's solution is measured out, 40 c.c. of water added and a 5 per cent. solution of potassium cyanide is run in carefully until it is just decolorised, the slightest excess of cyanide being avoided. 10 c.c. more of the Fehling's solution is now added and the titration with the sugar solution performed in the usual manner at a boiling temperature until the liquid is just decolorised. In this case only the second 10 c.c. of Fehling's solution is reduced and there is no precipitation of cuprous oxide, but instead the liquid loses its blue colour as the reduction proceeds (Sutton, "Volumetric Analysis," 17th ed., p. 317). See also Sachsses' solution and Knapp's solution.

Method of Verifying Fehling's Solution and Remarks on its Keeping Qualities.—According to Borntträger ("J.S.C.I.," 1893, p. 1063) Fehling's solution is standardised on a 0·5 per cent. solution of invert sugar, prepared as follows: 19 gms. pure saccharose are dissolved in water, 10 c.c. hydrochloric acid of 1·188 sp. gr. at 15°, or 20 c.c. of 1·10 sp. gr. added, and the solution made up to 100 c.c.

After allowing to stand over night, 25 c.c. of the solution, with a little litmus tincture added, are neutralised with alkali and diluted to a litre with water ; the resulting solution contains

0·5 gm. invert sugar in 100 c.c. It is most important that the inversion be conducted in the cold. A pure saccharose may be obtained by precipitating a filtered solution of refined beet sugar with alcohol in the cold, washing with absolute alcohol and drying.

With regard to the keeping qualities of Fehling's solution the author can corroborate, from personal experience, the following observations by Bornträger ("Zeit. f. anal. Chem.," 1895, p. 22, and "J.C.S.," 1895, A., ii., p. 187): "The changes which the mixed solution has been frequently observed to undergo are caused, as is well known, by the Rochelle salts, even an alkaline solution of which has often become useless after a time, and it is therefore advisable to renew it repeatedly. However, if before adding the caustic soda to the aqueous solution of the salt any particles of wood, etc., which may be floating about are filtered off, on now rendering alkaline the solution will remain unchanged for a long time, and on boiling with the copper solution will not precipitate the cuprous oxide. The mixture must be as free as possible from iron, since even traces produce a greenish colour at the end reaction, the ferrous oxide present being oxidised in contact with air, the small quantity of ferric oxide thus formed giving a colour reaction with the ferro-cyanide in presence of acetic acid. The caustic soda and Rochelle salts employed must be free from iron."

FORMALDEHYDE.—Formaldehyde (HCHO + Aq.). Mol. wt., 30·02. A saturated solution of formaldehyde in water, sp. gr., 1·08. Clear, colourless liquid, with a pungent odour.

Tests for Impurities.—*Acidity.*—Formaldehyde must be neutral, or only very faintly acid. 1 c.c. of the solution should show no acid reaction after adding 1 drop of normal alkali.

Sulphuric Acid, Chlorine, Metals.—On diluting the solution with 5 parts of water no reaction should take place with silver nitrate, barium nitrate, or hydrogen sulphide solution or ammonium sulphide.

Methyl Alcohol.—This is sometimes added to prevent the separation of trioxymethylene. According to Duyk ("J. Pharm. Chem.," 1902, 15 [2], pp. 69-70) commercial formaldehyde usually contains 3 to 4 per cent. of methyl alcohol. This

is estimated by converting the formalin into hexamethylene tetramine, distilling, concentrating the methyl alcohol in the distillate by fractionation and converting it into methyl iodide by the action of iodine and red phosphorus, the methyl iodide being subsequently obtained by fractionation and its volume measured.

Strength.—The liquid must contain 40 per cent. of formaldehyde by volume.

Qualitative Tests for Formaldehyde.—1. Add to 5 c.c. of the solution to be tested ·03 gm. of phenylhydrazine hydrochloride and 4 or 5 drops of a 1 per cent. solution of ferric chloride. In presence of formaldehyde a precipitate is formed which is soluble in alcohol. This reaction is capable of giving a reaction with 1 part of formaldehyde in 150,000. Acetic aldehyde and benzaldehyde give no reaction.

2. To 5 c.c. of the solution add a small piece of phenylhydrazine hydrochloride, 2 or 3 drops of a 10 per cent. solution of potassium ferricyanide, and 8 or 10 drops of a 12 per cent. solution of sodium hydrate. In presence of formaldehyde a green or bluish-green colour appears. This is capable of detecting 1 part of formaldehyde in 80,000. If instead of caustic soda about 5 c.c. of concentrated hydrochloric acid is added a rose-red colour is developed.

3. **Hehner's Method.**—Add to the solution to be tested a few drops of commercial hydrochloric acid (containing iron), a few drops of milk or other albuminous fluid, and then pour gently concentrated sulphuric acid down the side of the tube. A violet ring develops if formaldehyde is present.

4. **Jorissen's Method.**—Add to 10 c.c. of the liquid to be tested 2 c.c. of solution containing 1 gm. of phloroglucol and 20 gms. of sodium hydroxide in 100 c.c. of water. A bright red colour develops if formaldehyde is present.

Note.—Formaldehyde yields solid condensation products with phenols and concentrated sulphuric or hydrochloric acids. Used as artificial resins and as insulating materials under the name of *Baekelite*. This reaction may be used as a test for formaldehyde, thus a solution containing a trace of formaldehyde on mixing with a little phenol and then pouring concentrated sulphuric acid down the side of the tube so as to form a lower layer, a rose-red ring surmounted by a whitish cloud is developed.

Quantitative Estimation.—For quantitative estimation a known excess of normal ammonia is added, and after several hours' standing the solution is titrated with normal sulphuric acid, using rosolic acid as indicator. The reaction depends on the formation of hexamethylene tetramine. Six molecules of formaldehyde correspond to four molecules of NH_3. An exact description of the analysis is given by Bird, "J.S.C.I.," 1896, p. 833. Several articles on the quantitative estimation of formaldehyde have appeared of late in consequence of the uncertain results obtained from the methods proposed. Reference to this point is given, *inter alia*, in "Pharm. Ztg.," 1895. H. Luttke ("Pharm. Zeit.," 1893, 38, p. 281. B. H. Smith, "J. Amer. Chem. Soc.," 1903, 25, pp. 1028-1035. O. Blank and H. Finkenbeiner, "Ber.," 31, p. 2979).

Uses and Storage.—Formaldehyde has recently been adopted for hardening and preserving animal tissues and gives good results. On the sterilisation of cellars, etc., by means of formaldehyde vapour, see an article by Windisch, abst. "J.S.C.I.," 1895, p. 290. Formaldehyde should be stored in stoppered bottles, kept in a cool place.

Commercial Varieties.—The solution is also sold under the name of "Formal" and "Formalin," containing 35 to 40 per cent. formaldehyde. These often contain methyl alcohol which is added to prevent the separation of solid trioxymethylene.

FLUORESCEÏN.—Resorcinphthaleïn, $C_{20}H_{12}O_5$. Red crystals, insoluble in cold water, slightly soluble hot, soluble in alcohol with a red colour and green fluorescence, also soluble in ether.

Uses.—After reduction with zinc and caustic potash is employed as a test for blood. C. Fleig (Merck's "Annual," 1910, p. 189).

FUCHSINE.—Rosaniline hydrochloride ($C_{20}H_{19}N_3HCl$). Mol. wt., 337·75, formerly known as Azaleine, Magenta, Rubine, etc. Large, stable, beetle-green crystals, giving an intensely magenta-red solution in alcohol. It is a valuable stain, much used in bacteriological investigations; it dyes wool, silk, and

leather without a mordant, but with cotton a mordant consisting of tannin and tartar emetic has to be employed.

Tests for Impurities.—The general appearance of the sample is, as a rule, a sufficiently good indication of its purity, but for use as a stain only the purest commercial quality must be used —namely, the well-crystallised quality, or the variety known as "diamond" fuchsine (the preparation of fuchsine solution is described under "Reagents in Solution" in the appendix). Arsenic, traces of which are sometimes present, may be detected by a method recommended by Fresenius and Hintz ("J.S.C.I.," 1888, p. 456). Marsh's test may also be used, the sample being previously ignited with a little soda, and the residue dissolved.

Mineral impurities can be detected after ignition. Pure fuchsine in solution is almost completely decolorised by sulphurous acid, while impure samples are rendered yellow and brown. In practice the colour is tested by performing a dyeing experiment (Allen, "Comm. Organ. Anal.," vol. iii., pt. i., p. 388). Fuchsine dissolves in hydrochloric acid, forming a yellow solution. Only the purest diamond fuchsine should be used for analytical purposes, and the solution should be gently warmed and filtered.

Uses.—In addition to the uses mentioned above, fuchsine has been proposed as a test for chlorine and bromine (I. Guareschi, "Chem. Zentral.," 1912, p. 635; "J.S.C.I.," 1912, p. 1149; Denigès and Chelle, "Compt. Rend.," 1912, 721, p. 1010; "J.S.C.I.," 1912, p. 1078).

Commercial Varieties.—The acetate of rosaniline is sometimes found in the market under the name of "fuchsine," and in addition to the pure crystallised qualities mentioned above, samples in small crystals can be obtained. The impure products in the form of an amorphous powder, or in large, irregular lumps, are called "grenat," "scarlet," etc.

Acid Fuchsine. — Commercial acid fuchsine, called also Fuchsine S and Rubine S, differs from the ordinary fuchsine in composition, being the sodium or ammonium salt of rosaniline trisulphonic acid. Its aqueous solution is bluish-red, it is nearly insoluble in alcohol, and is not acted upon by hydrochloric acid. It dyes wool and silk from an acid bath, has only half the dyeing power of fuchsine, and is useless for

cotton. It is used in the formation of certain staining solutions, e.g., the methyl-green orange-acid fuchsine of Biradi. On the fibre, fuchsine and fuchsine S have about the same tint, but can be distinguished by heating the coloured fibre with a mixture of equal parts of hydrochloric acid and water; fuchsine is decolorised, but acid fuchsine is practically unaffected; sufficient, however, is dissolved to render the solution magenta-red.

See also "Schiff's Reagent".

FURFUROL.—Furfurol, puriss. pro analysi (C_4H_3O, COH). Mol. wt., 96·06. A limpid, colourless liquid, slightly soluble in water, mixes easily with alcohol and ether. Sp. gr., 1·165. B.p. 162° C.

Uses and Storage.—Furfurol is officially recognised in Germany as the test reagent for the prescribed admixture of sesame oil with margarine butter and margarine cheese. On its use as a test for sesame oil, see Allen's "Comm. Organ. Anal.," vol. ii., part. i., p. 145.

The above preparation is supplied by Messrs. E. Merck in hermetically sealed tubes owing to its liability to become coloured through the action of light and air.

GALLEIN.—Gallein (pyrogallol-phthalein), $C_{20}H_{10}O_7$, mol. wt., 362·18, according to Dechan, is a sensitive indicator giving a pale yellow-brown colour in neutral solution, and turning rose-red on addition of a slight excess of alkali. Its degree of sensitiveness is recorded in the table of Indicators, p. 142, but it is rarely used. Its properties are described in Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 73.

GALLEIN, $C_{20}H_{12}O_7$. — Oxidation product of pyrogallol-phthaleïns. Red-brown powder soluble in alcohol, forming a brown solution which becomes violet on addition of an alkali.

GALLIC ACID.—Acid. gallic. pur. albiss. cryst. Trihydroxybenzoic acid, ($C_6H_2(OH)_3CO_2H + H_2O$). Mol. wt., 188·12. M.p. commences at 220°. Fine, silky, colourless or nearly colourless needles, soluble in 100 parts cold water, easily soluble in alcohol, slightly soluble in ether. A solu-

tion of glue gives no precipitate with gallic acid, but with a very dilute solution of ferric chloride a bluish-black precipitate forms.

Tests for Impurities.—*Non-Volatile Matter.* — After the ignition of 1 gm. on platinum foil no residue must remain.

Solubility.—The hot aqueous solution (1 : 20) must be clear and colourless, or have only a slight yellow tinge. On cooling the solution a crystalline precipitate of gallic acid is thrown down.

Sulphuric Acid —The solution in hot water (1 : 50) must not show a turbidity on addition of barium chloride solution and a little hydrochloric acid.

Tannic Acid.—Gallic acid gives no precipitate with gelatin solution or with starch.

Potassium cyanide gives a reddish colour with gallic acid but none with tannic acid (Young's test).

Uses.—It is sometimes used in the detection of iron salts (in mineral water) and free mineral acids (Flückiger).

Commercial Varieties.—It can be obtained in the market in a very pure state. Its properties are exhaustively described in Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 66.

GLYCEROL, GLYCERIN.—Propantriol, $C_3H_5(OH)_3$. Mol wt., 92·08. Sp. gr., 1·26. Clear, colourless, syrupy liquid.. When anhydrous b.p. 290°.

Tests for Impurities.—*Free Acid.*—The liquid after dilution should give no reaction with litmus paper.

Organic Residue.—Polyglycerols are estimated by gently heating the glycerin in an open dish at 160°.

Mineral Residue.—On heating at a higher temperature there should be only a minute trace of ash left.

Arsenic.—The glycerin should be absolutely free from arsenic.

Lime, Iron.—These may be tested for in the ash.

Chlorine.—The glycerin after dilution should give no cloudiness with silver nitrate. Other impurities such as acrolein, butyric acid, and trimethyleneglycol may occur.

Sugar.—Sugar and glucose are sometimes used as adulterants when glycerin is high in price. It may be estimated

by a polariscopic examination. The glycerin should give no reduction with Fehling's solution even after heating with HCl.

Quantitative Estimation.—In reasonably pure glycerin the amount of glycerol can be estimated by the specific gravity or by examination with the refractometer. In impure glycerols it is determined either by the acetin or bichromate methods (Lewkowitsch, "Technology of Oils, Fats, etc.," 1915, vol. iii., p. 382 *et seq.*).

Uses and Storage.—Glycerin is used as a qualitative test for borax, also in the quantitative estimation of borax and boric acid for which purposes it should be free from acid. As it absorbs water from the atmosphere it should be kept in stoppered bottles. On the large scale it is sent out in iron drums holding 5 to 10 cwt.

Commercial Varieties.—Chemically pure glycerin has a sp. gr. of 1·26. Other chemically pure glycerins have sp. gr. of 1·25, 1·24. Distilled glycerin or dynamite glycerin should have a sp. gr. of 1·261 at 15·5° C. Should be free from acid, lime, magnesia, and alumina. Should not contain more than a trace of chlorine, or a minute trace of arsenic, and the total residue should not be more than 0·25 per cent.

There are many varieties of distilled glycerin varying in colour from deep yellow to almost colourless. These are employed for commercial purposes. Crude glycerin or evaporated glycerin contains large quantities of salts, mostly common salt.

GOLD CHLORIDE.—Aurum chloratum, pur.: chloroauric acid ($AuCl_3$, HCl, $4H_2O$). Mol. wt., 412·11. Yellow hygroscopic crystals, easily soluble in water and alcohol.

Tests for Impurities and Quantitative Estimation.—The salt is ignited, the metallic gold remaining is then treated with nitric acid, and weighed; the impurities present may be determined in the acid washings. According to Post ("Chem.-technische Untersuchungen," 2nd ed., vol. i., p. 667) the best method of analysing the salts of gold is as follows: The gold in the chloride and the double salt with ammonium is estimated by simple ignition if no other metals are present. The salt is heated carefully for some time in a weighed porcelain crucible (the heating being conducted gently at first) till all

the water or ammonium chloride has been driven off: the heating may now be increased until the pure metal is left behind. Sodio-gold chloride may be ignited after addition of oxalic acid, metallic gold and sodium chloride being formed: the former may then be dried and weighed after the sodium chloride has been removed by washing. In presence of other metals a weighed quantity of the salt is dissolved in water, a little hydrochloric acid added, and the metallic gold precipitated with a solution of ferrous sulphate, ferrous chloride, or oxalic acid. The other metals are estimated in the filtrate.

Uses and Storage.—Gold chloride is used in microscopical investigations for staining cells and for toning photographic prints and must be kept in well-stoppered bottles. *Böttger's Ozone Paper* consists of filter paper saturated with acid-free gold chloride solution, and is used as a test for ozone, the presence of which produces a violet colour.

Commercial Varieties.—There are two kinds of gold chloride: (1) the yellow chloride, and (2) the brown chloride of gold, the latter being formed by concentrating the yellow salt.

The pure yellow salt ($AuCl_3$, HCl, $4H_2O$) contains about 48 per cent. metallic gold. Commercial samples sometimes show a somewhat higher percentage (about 50 per cent.), owing to less water being present. In addition to the above preparations the sodio-gold chloride is found in the market in several varieties. The salt of the German Pharmacopœia leaves a residue of from 30 to 30·8 per cent. pure gold on ignition and treatment with water. It is a dry crystalline powder of a golden-yellow colour.

GRAPE SUGAR.—See under "Sugar".

GUAIACOL.—Mono-methyl ester of pyrocatechin. $C_6H_4(OH)(O.CH_3)$. Mol. wt., 124·1. Yellowish crystals. M.p., 31°. B.p., 205°.

Uses.—Yields a green colour with ferric chloride.

May be used as a test for oxydases in the same way as tincture of guaiacum but yields a pale reddish colour.

According to K. Schern and W. Schellhase (Merck's "Annual," 1912, p. 209) fresh tincture of guaiacum is not very

sensitive, but it is rendered more delicate by adding a few drops of hydrogen peroxide. Old tincture of guaiacum however is satisfactory. These authors prefer to employ a mixture of tincture of guaiacum and guaiacol, and give the following quantities for the preparation of the reagent:—

Guaiacum resin	10 grams
Guaiacol	10 grams
Hydrogen peroxide	1 drop
Absolute alcohol	80 grams

This reagent poured upon unboiled milk gives a deep blue ring, below which there is usually a pale reddish ring visible. With boiled milk there is no reaction.

GUAIACUM, TINCTURE OF. — According to Schär ("Pharm. Ztg.," 1894, p. 675) tincture of guaiacum is best prepared from the pure resin (1 : 50 or 1 : 100) as guaiac wood is not so suitable, tannic acids being dissolved out at the same time. It is used for three purposes: (1) the detection of ozone, and such substances as show the reactions of ozonised oxygen i.e., oxidases; (2) as a test for blood; (3) the detection of copper or cyanogen compounds. For details regarding the preparation of the tincture, see loc. cit., or "Chem. Ztg.," 1894, p. 1516. The active principle of the resin is guaiaconic acid, which is coloured an intense ultramarine blue by the action of ozonised oxygen. The tincture, prepared either with alcohol, ether, or chloroform, must be kept in the dark, otherwise it loses its property as a reagent. See an article on guaiacum resin by Doebner and Lücker, "J.C.S.," 1897, A., pt. i., p. 165. See also Guaiacol.

HAEMATOXYLINE.—Haematoxylin pur. cryst. ($C_{16}H_{14}O_6$, $3H_2O$). Mol. wt., 356·17. Bright, pale yellow prisms, soluble in ether, alcohol, and hot water. It melts at 100° to 120° with loss of water.

Tests for Impurities.—Haematoxyline is tested for "solubility," and must dissolve in ether to a clear solution. It must also leave no residue after ignition on platinum foil, and the crystals must have the appearance described above. It dissolves in ammonia, producing a purple colour.

Uses and Storage.—The haematoxyline staining solution is extensively used in microscopy, and the alum-haematoxyline solutions of Boehmer, Frey, and others may be referred to here; these are prepared by well-known methods. Haematoxyline is readily soluble in a saturated solution of borax, and the ammonium present in the atmosphere soon colours it red. It may even become red from absorption of alkali from the glass bottles in which it is kept, and as sunlight also produces the same effect it must therefore be very carefully preserved in the dark.

Haematein, Haematoxyline Solution and Haematoxyline Paper.—All haematoxyline solutions (see above) must first ripen before they are fit for use, i.e., the formation of haematein must first take place through the action of air and light. Haematein ($(C_{16}H_{12}O_6)$, a brown powder) and its ammonium compound (dark violet crystals) are used in place of haematoxyline for the preparation of these solutions. It is difficult to prepare perfectly soluble haematein. The ammonium salt is prepared by dissolving 1 part of haematoxyline in 20 parts of warm water, adding 1 part of ammonia and allowing the solution to evaporate spontaneously in a large shallow basin. Detailed descriptions of haematoxyline solutions are given in Bolles Lee's "Microtomist's Vade Mecum," 4th ed., p. 161 *et seq.*, and the method of ripening these solutions is also given there.

Haematoxyline also finds use as an indicator for various substances, as, for example, the salts of copper, also for the detection of alum, but its use in acidimetry and alkalimetry is not possible. Logwood may be used in lieu of haematoxyline in preparing the indicator (Mohr, "Titrirmethode," 6th ed., p. 84; and also Cohn, "Indicators and Test Papers," p. 82 *et seq.*).

Haematoxyline Paper is also used in the laboratory; it is white or yellowish-white, but as it is coloured blue by the ammonia in the atmosphere it is difficult to preserve unchanged. The paper used in its preparation must first be freed from carbonate of lime by treatment with hydrochloric acid and water.

HEXAMETHYL-p-AMINO-TRIPHENYLMETHANE.—Hexamethyl-p-amino-triphenylmethane serves as a delicate

test for free chlorine and is especially valuable in the testing of potable waters which have been sterilised with hypochlorites for detecting excess of the reagent. In an acid solution it gives a violet colour if free chlorine is present. It will detect 3 parts of free Cl in 100,000,000 parts of water.

HYDRAZINE SULPHATE. — Hydrazinum sulfuricum. $NH_2 . NH . H_2SO_4$. Mol. wt., 129·12. White crystalline powder, soluble in water.

Uses.—May be employed for the detection of nitric acid in presence of nitrous acid. When added to a solution containing the two acids, the nitrous acid is decomposed into nitrogen and ammonia whereas the nitric acid is unaffected and can subsequently be detected by diphenylamine (Hemendra Kumar Sen and Biman Bihary Dey, "Zeits. für anorg. Chem.," 1912, p. 52; Merck's "Annual," 1912, p. 231). On the action of hydrazine on ferricyanide and on a new method of estimating hydrazine and ferricyanides, see P. R. Ray and H. K. Sen, "Z. anorg. Chem.," 1912, 76, pp. 380-386; "J.S.C.I.," 1912, p. 719.

Hydrazine salts act as powerful reducing agents in presence of certain metallic compounds, converting chlorates into chlorides (which may then be estimated), (W. R. Hodgkinson, "J.S.C.I.," 1914, p. 815).

On the use of hydrazine sulphate in the volumetric estimation of mercury, see W. Stürve ("Chem. Zeit.," 1914, 38, p. 320; "J.S.C.I.," 1914, p. 891).

HYDRIODIC ACID.—Acid. hydriodicum, pur. (HI). Mol. wt., 127·93. The solution in water is a colourless liquid, quickly turning yellow in contact with air, through absorption of oxygen. Sp. gr., 1·56 containing about 52 per cent. of the acid.

Tests for Impurities.—*Residue.*—On ignition of 5 gms. only traces of residue should remain behind.

Metals and Earths.—10 gms. are diluted with 100 c.c. of water and hydrogen sulphide passed; no coloured precipitate should appear; the addition of ammonia and ammonium sulphide must also leave the solution unaltered.

Hydrochloric and Hydrobromic Acid.—A simple method of ascertaining whether large quantities of the above acids are present is to neutralise with pure caustic potash, evaporate to dryness, and, after grinding and drying the potassium iodide so obtained, to digest with 12 parts of 92 per cent. spirits of wine, in which the iodide dissolves completely. Potassium bromide, and particularly potassium chloride, are both difficultly soluble in alcohol, as is well known; thus the larger portion of either salt would remain undissolved.

Note.—The fact that chloride of silver is readily soluble in ammonia, bromide of silver much less so, and the iodide practically insoluble, presents a method of detecting hydrochloric acid. The dilute hydroidic acid solution is precipitated with silver nitrate, ammonia added in excess, and the mixture shaken and filtered; if the filtrate shows a precipitate on addition of nitric acid in excess, hydrochloric acid is present. No notice must, however, be taken of a slight turbidity. On the detection of chlorine and bromine in iodine compounds, see under "Iodine" and "Potassium Iodate".

The quantitative estimation of hydrochloric acid and hydrobromic acid, appearing as impurities, is treated of in Fresenius, "Quant. Anal.," vol. i., p. 511.

Sulphuric Acid.—Tests as under "Hydrobromic Acid," p. 122.

Quantitative Estimation.—The percentage is found either from the specific gravity or by titration with alkali.

Sp. Gr. of Hydriodic Acid at 15° (Wright).

Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.
1·000	0	1·187	20	1·438	40
1·045	5	1·239	25	1·533	45
1·091	10	1·296	30	1·650	50
1·138	15	1·361	35	1·700	52

Other methods for the quantitative estimation of hydriodic acid are described in Fresenius, "Quant. Anal.," 7th ed., vol. i., p. 365 *et seq.*; also under "Potassium Iodide" in this book.

Uses and Storage.—As a strong reducing agent the acid is used for numerous organic syntheses, and is recommended by Kuhlmann for the detection of nitrous acid ("Repertor. d. Chem.-Ztg.," 1888, p. 269).

R. Benedikt ("J.S.C.I.," 1892, p. 181) employs hydriodic acid of 1·70 sp. gr. in the analysis of lead sulphate; the acid must be carefully preserved in the dark.

Commercial Varieties.—These as a rule have densities ranging from 1·50 to 1·70, and are generally of a yellow colour, owing to absorption of oxygen; this decomposition, caused by atmospheric oxygen, may readily occur in dilute or concentrated solutions, the iodine liberated remaining in solution until, through further decomposition, the point of saturation is reached, when it crystallises out. The author has failed to find adulterated commercial samples.

HYDROBROMIC ACID.—Acid. hydrobromic. puriss. (HBr). Mol. wt., 80·93. The solution in water is a clear, colourless, liquid—sp. gr., 1·78 (82 per cent.), sp. gr. usually about 1·38—containing about 40 per cent. HBr.

Tests for Impurities.—*Residue.*—10 gms. must leave no weighable residue on evaporation.

Note.—On the estimation of the residual matter, see also under "Hydrochloric Acid," p. 124.

Sulphuric Acid.—5 gms. on dilution with 50 c.c. of water and addition of barium chloride should show no reaction after 12 hours' standing.

Note.—Sulphuric acid can also be detected on evaporation of the hydrobromic acid, after the same method as that described under "Hydrochloric Acid," p. 112.

Heavy Metals, Arsenic, Alumina, and Lime.—As under "Hydrochloric Acid," p. 123.

Hydrochloric Acid.—2 drops of the acid are diluted with 4 c.c. of water and silver nitrate solution added; after shaking, 6 c.c. of ammonium carbonate solution are added; the mixture is then heated for a few minutes and filtered. The clear filtrate must show only a slight turbidity on addition of nitric acid in excess (see note under "Bromine," p. 59).

Iodic Acid and Iodine.—To 5 drops of the acid are added 5 c.c. of water, 5 c.c. of ammonia (0·960) and 1 drop of nitrate of silver solution. On shaking, the mixture must remain clear, or only so slightly turbid that the liquid is still transparent.

The test can also be conducted as under "Bromine," p. 59.

Quantitative Estimation.—A pure hydrobromic acid solution may be estimated volumetrically, or its strength may be gauged by the specific gravity.

Sp. Gr. of Hydrobromic Acid at 15° (Wright).

Sp. Gr.	HBr. Per Cent.	Sp. Gr.	HBr. Per Cent.	Sp. Gr.	HBr. Per Cent.
1·000	0	1·159	20	1·365	40
1·038	5	1·204	25	1·445	45
1·077	10	1·252	30	1·515	50
1·117	15	1·305	35		

For quantitative estimation of bromides, see under "Potassium Bromide".

Uses and Storage.—Hydrobromic acid, even when slightly concentrated, dissolves all native and artificial monsulphides of the metals, mercury, copper, and lead being dissolved with copious evolution of hydrogen. It is supposed to be specially adapted for the estimation of sulphur ("J.S.C.I.," 1884, p. 23), and towards organic compounds it behaves much in the same way as hydrochloric acid. It should be kept in a cool place, protected from light, and is poisonous.

Commercial Varieties.—Samples of varying specific gravities (up to 1·49) are found in the market, and the so-called "Fothergill hydrobromic acid" is employed in medicine. It often contains considerable quantities of potassium bitartrate, and must not be confounded with the acid used for analytical purposes ("Pharm. Ztg.," 1888, p. 25).

HYDROCHLORIC ACID.—Acidum hydrochloric. pur. conc. (HCl). Mol. wt., 36·47. The solution of the gas in water has a sp. gr. 1·19. The acid must be clear and colourless, and must not emit any smell on dilution with water.

100 parts by weight of this acid contain 37·23 parts HCl (31·79 British Pharm.).

Tests for Impurities.—*General Appearance, Odour, etc.*—See above.

Sulphuric Acid.—(*a*) 5 gms. are diluted with 50 c.c. of

water and barium chloride added; after 12 hours' standing no precipitate must appear.

(*b*) 100 gms. should contain no sulphuric acid or only a maximum amount of 0·0005 gm. For this test 500 gms. are slowly evaporated on a water bath to 1 c.c. and sulphuric acid is estimated in the residue, if present.

Note.—On testing several samples of commercial hydrochloric acid puriss. a few years ago, the author found scarcely a single sample perfectly free from sulphuric acid, and this after making a careful quantitative estimation by the above method. Several samples showed the sulphuric acid reaction in the ordinary way of testing, namely, on dilution with water, without evaporation of the acid. In the pure commercial preparation the amount of sulphuric acid ought to be very small, and the author has added the above quantitative method of testing in order to fix a limit. The pure acid now sold generally answers the above test, and owing to the recognition paid to the more stringent conditions by the manufacturers, impure varieties are now very seldom found.

Regarding the detection of sulphuric acid the investigations of Biltz ("Arch. d. Pharm," 1874, ii., p. 149 *et seq.*) may be indicated here. According to that author, acetic acid and the acetates interfere least with the barium reaction; on the other hand, hydrochloric and nitric acids and the nitrates in acid solution have the principal disturbing influence on the reaction; between these two classes come the nitrates in neutral solution.

Residue.—10 gms. must leave no weighable residue on evaporation in a platinum capsule.

Note.—On evaporating large quantities of pure concentrated hydrochloric acid, in nearly every case traces of residue remain. The author generally obtained about one milligramme of residue on evaporating 50 gms. in a porcelain basin (see also note under "Nitric Acid"). Good commercial samples contain only traces of impurities, so that these may be disregarded in most cases in using the acid for analysis; notwithstanding, it is a matter of importance to call attention to these traces, and the quantities to be taken for the estimation of the volatile matter and sulphuric acid have been stated in order that poor or less carefully prepared commercial samples (often sold as pure) may be more easily recognised than hitherto. It is well to mention in addition to the above notes, which have been taken from the second edition of this book, that, as already mentioned, mineral acids are generally found of late to be of a purer quality than formerly; this not only applies to hydrochloric acid, but also to nitric acid and sulphuric. In the better commercial samples of hydrochloric acid a residue, on evaporation of even large quantities in a platinum capsule,

can scarcely be detected. If a residue is found, it may be due to storage of the acid in inferior glass bottles, as certain kinds of glass are strongly corroded ("J.C.S.," 1892, A., pp. 410, 411).

Arsenic, Heavy Metals, Alumina, and Lime.—(*a*) 10 gms. are diluted with 10 c.c. of water in a test tube, and 5 c.c. freshly prepared H_2S water carefully introduced so as to form a layer on the surface; on standing for 1 hour in either a warm or cool place no colour must appear, and no yellow ring at the point of contact.

The test for arsenic in Marsh's apparatus should also be made as a check, using 50 gms. of the acid, previously evaporated down with a trace of potassium chlorate as recommended subsequently. Hydrogen is then produced, as described under "Sulphuric Acid" and "Zinc," after which the liquid to be tested is introduced; after the test has been in action half an hour, only a very slight trace of deposited arsenic should appear in the tube, which must not take the form of a distinct mirror.

Note.—It is possible in the case of pure commercial sulphuric acid (and also pure zinc) to guarantee the absence of every trace of deposit in the Marsh test, but in the case of hydrochloric acid the manufacturers cannot give this guarantee; exception, however, must not be taken to a very slight deposit. The author has tested the pure acid obtained from the best sources, in the above way, and has nearly always found a small deposit in the tube. Even on testing the pure acid prepared from very pure well-grown crystals of sodium chloride by the action of sulphuric acid, absolutely arsenic-free, he obtained a small trace of deposit in the Marsh test, although the same acid (and the afore-mentioned pure commercial samples) proved to be perfectly free from arsenic on testing with H_2S, or by Gutzeit or Lohmann's method (see later). Pure hydrochloric acid, as it is now put on the market, is quite good enough for most laboratory purposes. For forensic investigations an acid is sometimes demanded which is perfectly free from arsenic, which does not give a reaction in Marsh's test, even after evaporation of large quantities (several litres), with the addition of potassium chlorate. Such acid is best obtained, according to Otto and Beckurts, by treating the ordinary acid with a sufficiency of H_2S or iron perchloride, and then redistilling ("J.S.C.I.," 1886, pp. 534, 602). A number of other methods have been proposed for preparing this special acid (see "Pharm. Ztg.," 1897, p. 276; "J.S.C.I.," 1897, pp. 43, 466, 680), but comparative investigations must first prove that it is possible by these methods to really obtain a preparation on a large scale which can be guaranteed

free from the slightest deposit in the Marsh apparatus. With reference to this test Otto ("Ausmittelung der Gifte," 1884, p. 146 *et seq.*, Vieweg, Brunswick) recommends that a certain quantity of the acid should be evaporated in a good porcelain basin on the water bath, with the addition of a few crystals of potassium chlorate, and, if necessary, sufficient water to reduce the specific gravity if above 1·104; the residue is then diluted and tested. Otto also mentions (loc. cit., p. 167 *et seq.*) precautions to be observed in performing Marsh's test (see also under "Iron Perchloride," test for arsenic). Regarding other methods for detecting traces of arsenic, several of which are based on the formation of arseniuretted hydrogen, the latter being detected, not by the above test, but by the reaction with silver nitrate or mercuric chloride solution, exhaustive investigations of a comparative nature have been published by Flückiger, "Arch. d. Pharm.," 1889, p. 1 *et seq.* (see also "J.C.S.," 1889, A., p. 650). From his experiments Flückiger finds that of all the methods examined, Gutzeit's is the most reliable, giving a very sharp reaction. The process is as follows: 1 gm. of chemically pure zinc, and 4 c.c. of 7 per cent. hydrochloric acid are put into a narrow-necked flask of 50 c.c. capacity; into the neck of the flask (which should be about 1½ c.m. wide), two discs of filter paper are fixed, to retain any moisture carried over by the liberated hydrogen; the mouth of the flask is covered by a piece of filter paper, previously moistened with a drop of saturated silver nitrate solution acidified with a little nitric acid. The test must be performed in a dimly-lighted room, and, after 1 or 2 hours' standing, no yellow or black stain must appear on the spot moistened with the silver solution; a yellow stain, turning to black through absorption of moisture, shows the presence of arsenic.

According to Poleck and Thummel, the reaction which takes place between the arseniuretted hydrogen and the strong solution of silver nitrate is represented as follows:—

$$AsH_3 + 6NO_3Ag = 3NO_3H + AsAg_3(NO_3Ag)_3.$$

The yellow compound so produced is decomposed by water, thus:—

$$AsAg_3(NO_3Ag)_3 + 3H_2O = 3NO_3H + As(OH)_3 + 6Ag.$$

In conducting this test several precautionary measures have to be observed, particular care being taken to ensure a slow evolution of hydrogen. As H_2S, PH_3 and SbH_3 have the same effect on the silver nitrate paper, perfectly pure zinc must be used, and the hydrochloric acid must either be free from SO_2, or its removal must be effected beforehand, e.g., by bromine. If all these precautions are not taken, it is an easy matter to obtain erroneous results by Gutzeit's method (see "Pharm. Ztg.," 1889, p. 275; and the articles by Flückiger, loc. cit., also Otto, loc. cit., p. 147). These references also prove that the method adopted in the German Pharmacopœia (ii.), of conducting Gutzeit's test, leads to incorrect results. To avoid error in executing

this test, according to Curtmann ("Pharm. Ztg.," 1891, p. 114; see also "Analyst," 1891, p. 237), it is necessary to have an atmosphere free from coal-gas, or any gas employed for lighting purposes, and the papers—particularly the thicker ones—must be free from dust, and must not be kept in a room where the said gases can have access to them. Ordinary paper containing woody fibre is quite unreliable. Lohmann ("Pharm. Ztg.," 1891, p. 748 *et seq.*) also confirms the unreliable nature of Gutzeit's test on the ground that the paper moistened with silver nitrate is sometimes coloured when arsenic is not present, and recommends the use of mercuric chloride, as advocated by Flückiger. Lohmann considers that the use of mercuric chloride renders the test a very reliable one, and, although less delicate in its action than silver nitrate, is an improvement on Marsh's test. Unlike silver nitrate, the mercury salt is quite unaffected by air, light, or moisture. Lohmann describes the test as follows :—

A piece of filter paper is moistened with a drop of a saturated alcoholic solution of mercuric chloride, and in this case it is advisable to use paper which has been washed with hydrochloric and hydrofluoric acids. When the alcohol on the surface has evaporated, a second drop is added and allowed to evaporate, slight application of heat being permissible, and this process is repeated four or five times. The paper so prepared is now exposed to the action of the gas, for which purpose an Erlenmeyer flask of at least 400 c.c. capacity is used, the flask being closed with an india-rubber cork, into which a small funnel is inserted; this is covered with the prepared paper. The acid to be tested is now introduced into the flask along with some pure zinc, the height of liquid not being allowed to exceed 2·5 c.m. Even when greatly diluted, arseniuretted hydrogen forms a distinct yellow stain with corrosive sublimate; even in the presence of very small traces of arsenic a faint but distinct yellowish-red colour appears. Very dilute antimonietted hydrogen does not change the colour of the mercuric chloride, but if a sufficiently large quantity is present a brown stain results. For details of the method, see Lohmann, loc. cit. It may be remarked that the zinc used for the test must be free from sulphur and phosphorus, otherwise the mercuric chloride is affected. The author has tested the pure zinc for analysis, and the pure hydrochloric acid of the same description (manufactured by Messrs. E. Merck) by Lohmann's method, no reaction being obtained, but, on addition of only a few drops of crude commercial hydrochloric acid, containing arsenic, to the pure acid, the well-known yellow colour appeared at once.

Among other methods of detecting arsenic, less delicate than the above, Schlickum's test with sodium sulphite and tin chloride may be mentioned ("Chem. Industrie," 1886, p. 92; "Analyst," 1886, p. 19). By this test, 1/20 mgm. can be detected; Gutzeit's test shows 1/1000 mgm. Further, there is Bettendorf's method, consisting in heating

to boiling 7 c.c. to 8 c.c. of fuming acid in a test tube with about 1 gm. tin chloride; in presence of strong traces of arsenic, a brown coloration, or a brown precipitate of the metal itself, is formed, as, for example, in the case of raw hydrochloric acid, where much arsenic is present. According to the German Pharmacopœia (iii.), hydrochloric acid is tested for arsenic as follows: To 1 c.c. of the acid are added 3 c.c. stannous chloride solution (5 parts crystallised stannous chloride mixed to a paste, with 1 part hydrochloric acid, and dry gaseous acid passed through the liquid till saturated, and the liquid filtered); no coloration must take place within an hour. For the preparation of stannous chloride solution, see Appendix.

(*b*) 20 gms. of the acid are diluted with water, a slight excess of ammonia added, then a few drops ammonium sulphide and oxalate of ammonia; even on long standing no change should take place, particularly no dark coloration (heavy metals, etc.).

(*c*) 5 gms. diluted to 25 c.c. should show no red colour on addition of a few drops of potassium thiocyanate solution (iron).

(*d*) 20 gms. are diluted with about 200 c.c. of water, the liquid is heated, and hydrogen sulphide passed through it for about 5 minutes; no precipitate of sulphides must form, even after standing for some time.

Sulphurous Acid.—On adding a few c.c. of the acid, diluted as at (*d*), to a little water previously rendered slightly blue with iodine and starch, the colour must not be discharged.

Chlorine.—A few drops of potassium iodide solution are added to 5 c.c. very dilute and freshly prepared starch solution, and then a little dilute sulphuric acid. On adding to this solution 1 c.c. hydrochloric acid, diluted as above, no blue colour must appear.

Hydrobromic Acid.—See "Commercial Varieties".

Quantitative Estimation. — Pure hydrochloric acid, previously diluted with water (1 : 100), is estimated gravimetrically by precipitation with silver nitrate, or volumetrically with normal alkali. The simplest method of estimation is to take the specific gravity (see the following table, p. 130). On the quantitative estimation of the acid with normal alkali, see also Lunge and Marchlewski ("J.S.C.I.," 1891, p. 541). The

above authors titrate with normal alkali previously standardised on normal acid, the latter having been standardised gravimetrically on silver nitrate or volumetrically on sodium carbonate.

Uses and Storage.—The acid dissolves metals, metallic sulphides, oxides, peroxides, and salts; it is therefore often used in quantitative and qualitative analysis. It is employed as a test for silver, and, in forensic chemical analysis, for the decomposition of organic substances, in conjunction with chlorate of potash. The acid must be stored in a cellar, in well-stoppered glass vessels.

Normal Hydrochloric Acid.—The solution must contain 36·47 gms.[1] of hydrochloric acid per litre, and is prepared by mixing the pure concentrated acid with water. The acid is first diluted to a specific gravity of 1·020, thus giving an acid slightly stronger than normal (41). The standardising is now completed gravimetrically as in making normal sulphuric acid, but in this case by precipitation with silver nitrate. For precautions to be observed see Sutton, "Vol. Anal.," 7th ed, p. 48. The strength may be determined volumetrically on dehydrated sodium carbonate; this method is also mentioned under "Normal Sulphuric Acid". The purest transparent Iceland spar may be used in place of sodium carbonate in this acidimetric method (see "Analyst," May, 1900, p. 137). For precautions to be observed in employing the above methods with litmus or methyl orange as indicator, see Lunge, "The Alkali-Makers' Handbook," p. 168.

Commercial Varieties.—Schröder calls attention to the fact that he has detected a disagreeable smell, and a too strong reaction with permanganate, even in pure hydrochloric acid; an acid with such defects evidently contains organic chlorides ("Arch. d. Pharm.," 85, p. 386). Lohmann ("Pharm. Ztg.," 1889, p. 275) found tin in a number of pure commercial samples. Hager ("Pharm. Ztg.," 1887, 32, p. 98) tests for hydrobromic acid, and gives a sharp method for its detection. A sample of acid containing chlorine is mentioned in "Pharm. Ztg.," 1888, p. 25, and "J.C.S.," 1890, pp. 289, 547. On the subject of

[1] See also note under "Normal Caustic Potash".

SPECIFIC GRAVITIES OF HYDROCHLORIC (LUNGE AND

Sp. G. at $\frac{15°}{4°}$ (in Vacuo).	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight Chemically Pure Acid Correspond to				
			Per Cent. HCl.	Per Cent. Acid of 18° B.	Per Cent. Acid of 19° B.	Per Cent. Acid of 20° B.	Per Cent. Acid of 21° B.
1·000	0·0	0·0	0·16	0·57	0·53	0·49	0·47
1·005	0·7	1	1·15	4·08	3·84	3·58	3·42
1·010	1·4	2	2·14	7·60	7·14	6·66	6·36
1·015	2·1	3	3·12	11·08	10·41	9·71	9·27
1·020	2·7	4	4·13	14·67	13·79	12·86	12·27
1·025	3·4	5	5·15	18·30	17·19	16·04	15·30
1·030	4·1	6	6·15	21·85	20·53	19·16	18·27
1·035	4·7	7	7·15	25·40	23·87	22·27	21·25
1·040	5·4	8	8·16	28·99	27·24	25·42	24·25
1·045	6·0	9	9·16	32·55	30·58	28·53	27·22
1·050	6·7	10	10·17	36·14	33·95	31·68	30·22
1·055	7·4	11	11·18	39·73	37·33	34·82	33·22
1·060	8·0	12	12·19	43·32	40·70	37·97	36·23
1·065	8·7	13	13·19	46·87	44·04	41·09	39·20
1·070	9·4	14	14·17	50·35	47·31	44·14	42·11
1·075	10·0	15	15·16	53·87	50·62	47·22	45·05
1·080	10·6	16	16·15	57·39	53·92	50·31	47·99
1·085	11·2	17	17·13	60·87	57·19	53·36	50·90
1·090	11·9	18	18·11	64·35	60·47	56·41	53·82
1·095	12·4	19	19·06	67·73	63·64	59·37	56·64
1·100	13·0	20	20·01	71·11	66·81	62·33	59·46
1·105	13·6	21	20·97	74·52	70·01	65·32	62·32
1·110	14·2	22	21·92	77·89	73·19	68·28	65·14
1·115	14·9	23	22·86	81·23	76·32	71·21	67·93
1·120	15·4	24	23·82	84·64	79·53	74·20	70·79
1·125	16·0	25	24·78	88·06	82·74	77·19	73·64
1·130	16·5	26	25·75	91·50	85·97	80·21	76·52
1·135	17·1	27	26·70	94·88	89·15	83·18	79·34
1·140	17·7	28	27·66	98·29	92·35	86·17	82·20
1·1425	18·0		28·14	100·00	93·95	87·66	83·62
1·145	18·3	29	28·61	101·67	95·52	89·13	85·02
1·150	18·8	30	29·57	105·08	98·73	92·11	87·87
1·152	19·0		29·95	106·43	100·00	93·30	89·01
1·155	19·3	31	30·55	108·58	102·00	95·17	90·79
1·160	19·8	32	31·52	112·01	105·24	98·19	93·67
1·163	20·0		32·10	114·07	107·17	100·00	95·39
1·165	20·3	33	32·49	115·46	108·48	101·21	96·55
1·170	20·9	34	33·46	118·91	111·71	104·24	99·43
1·171	21·0		33·65	119·58	112·35	104·82	100·00
1·175	21·4	35	34·42	122·32	114·92	107·22	102·28
1·180	22·0	36	35·39	125·76	118·16	110·24	105·17
1·185	22·5	37	36·31	129·03	121·23	113·11	107·90
1·190	23·0	38	37·23	132·30	124·30	115·98	110·63
1·195	23·5	39	38·16	135·61	127·41	118·87	113·40
1·200	24·0	40	39·11	138·98	130·58	121·84	116·22

ACIDS OF VARIOUS STRENGTHS.
MARCHLEWSKI.)

Per Cent. Acid of 22° B.	1 Litre Contains Kilograms.					
	HCl.	Acid of 18° B.	Acid of 19° B.	Acid of 20° B.	Acid of 21° B.	Acid of 22° B.
0·45	0·0016	0·0057	0·0053	0·0049	0·0047	0·0045
3·25	0·012	0·041	0·039	0·036	0·034	0·033
6·04	0·022	0·077	0·072	0·067	0·064	0·061
8·81	0·032	0·113	0·106	0·099	0·094	0·089
11·67	0·042	0·150	0·141	0·131	0·125	0·119
14·55	0·053	0·188	0·176	0·164	0·157	0·149
17·38	0·064	0·225	0·212	0·197	0·188	0·179
20·20	0·074	0·263	0·247	0·231	0·220	0·209
23·06	0·085	0·302	0·283	0·264	0·252	0·240
25·88	0·096	0·340	0·320	0·298	0·284	0·270
28·74	0·107	0·380	0·357	0·333	0·317	0·302
31·59	0·118	0·419	0·394	0·367	0·351	0·333
34·44	0·129	0·459	0·431	0·403	0·384	0·365
37·27	0·141	0·499	0·469	0·438	0·418	0·397
40·04	0·152	0·539	0·506	0·472	0·451	0·428
42·84	0·163	0·579	0·544	0·508	0·484	0·460
45·63	0·174	0·620	0·582	0·543	0·518	0·493
48·40	0·186	0·660	0·621	0·579	0·552	0·523
51·17	0·197	0·701	0·659	0·615	0·587	0·578
53·86	0·209	0·742	0·697	0·650	0·620	0·590
56·54	0·220	0·782	0·735	0·686	0·654	0·622
59·26	0·232	0·823	0·774	0·722	0·689	0·655
61·94	0·243	0·865	0·812	0·758	0·723	0·687
64·60	0·255	0·906	0·851	0·794	0·757	0·719
67·31	0·267	0·948	0·891	0·831	0·793	0·754
70·02	0·278	0·991	0·931	0·868	0·828	0·788
72·76	0·291	1·034	0·972	0·906	0·865	0·822
75·45	0·303	1·077	1·011	0·944	0·901	0·856
78·16	0·315	1·121	1·053	0·982	0·937	0·891
79·51	0·322	1·143	1·073	1·002	0·955	0·908
80·84	0·328	1·164	1·094	1·021	0·973	0·926
83·55	0·340	1·208	1·135	1·059	1·011	0·961
84·63	0·345	1·226	1·152	1·075	1·025	0·975
86·32	0·353	1·254	1·178	1·099	1·049	0·997
89·07	0·366	1·299	1·221	1·139	1·087	1·033
90·70	0·373	1·326	1·246	1·163	1·109	1·054
91·81	0·379	1·345	1·264	1·179	1·125	1·070
94·55	0·392	1·391	1·307	1·220	1·163	1·106
95·09	0·394	1·400	1·316	1·227	1·171	1·113
97·26	0·404	1·437	1·350	1·260	1·202	1·143
100·00	0·418	1·484	1·394	1·301	1·241	1·180
102·60	0·430	1·529	1·437	1·340	1·279	1·216
105·20	0·443	1·574	1·479	1·380	1·317	1·252
107·83	0·456	1·621	1·523	1·421	1·355	1·289
110·51	0·469	1·667	1·567	1·462	1·395	1·326

tar-like impurities see "Arch. d. Pharm.," 1887, p. 1064. See also notes, pp. 124-125.

HYDROCHLORIC ACID, COMMERCIAL.—In addition to the pure acid the market supplies a crude commercial hydrochloric acid, the following impurities contained in it being mentioned in the literature on the subject: Sulphurous anhydride, sulphuric acid, chlorine, bromine, iodine, hydrofluoric acid, arsenic, iron, lime, and the alkalies; according to L. v. Halle ("Pharm. Ztg.," 1897, p. 157), traces of mercury have also been found. Alcock ("Pharm. Post," 1888, No. 37, p. 587) often found large quantities of sulphuric acid in the common yellow commercial acid, one sample showing 3·34 per cent., another 9·97 per cent. H_2SO_4. The latter may be estimated gravimetrically as barium sulphate, and a simple method for its volumetric estimation is mentioned by Rürup ("J.S.C.I.," 1894, p. 904). The author calls attention to the fact that a high percentage of sulphuric acid is injurious for certain technical purposes; commercial hydrochloric acid should therefore not contain more than 1 to 1·5 per cent. SO_3.

The quantitative estimation of the arsenious acid present is sometimes of importance; Buchner ("J.S.C.I.," 1891, p. 460), in estimating the arsenious acid in a sample of the crude acid, found 592 gms. As_2O_3 in 100 kilograms of the acid. Other investigations on this point show lower figures ("J.S.C.I.," 1891, p. 575), 100 kilograms containing 0·7 to 10·4 gms. arsenic. It may be mentioned that a crude acid called "free from arsenic" may be obtained, containing very small traces of arsenic, and showing only a very slight mirror in Marsh's test. Kretschmar recommends the following method for the quantitative estimation of arsenic ("Chem.-Ztg.," 1891, p. 299): The well-diluted solution is nearly neutralised with carbonate of soda; ammonia and ammonium sulphide are then added, an excess of chemically pure hydrochloric acid; a strong current of H_2S is then passed through the liquid for 2 hours, the solution being kept warm on a water bath; at the end of the time stated precipitation is complete; this would not be the case before from 15 to 24 hours in the ordinary way. The arsenic sulphide is washed, dissolved in

caustic potash solution and chlorine gas passed, or, better still bromine added. The arsenic is then precipitated, from a slightly acid solution, with ammonia and magnesia mixture, and estimated as arseniate of magnesia, but this method of estimation may give rise to inaccuracies owing to the means of preventing volatilisation of some of the arsenic being insufficient if the precipitate be too strongly ignited, and if not sufficiently ignited, part of the substance may easily escape conversion. It is therefore better to proceed as follows: After having hastened the settling of the magnesia compound by means of vigorous stirring the precipitate is filtered, washed, and dissolved into a large platinum dish by washing the filter with very dilute nitric acid. It is then evaporated, dried, and, after igniting for a short time at a red heat, weighed.

HYDROFLUORIC ACID.—Acid. hydrofluoric. fumans. puriss. (HF) about 40 per cent. Mol. wt., 20·0. When placed in a test tube of 1 to 2 c.m. diam. the acid should appear colourless. It attacks glass strongly, and fumes in contact with air.

Note.—Sometimes the pure acid has a slight colour, evidently due to long standing in gutta-percha bottles.

Tests for Impurities.—*Residue.*—On volatilisation and ignition of 10 gms. in a platinum capsule only a barely weighable residue should remain.

Note.—A carefully prepared sample ought only to give 1 to 2 mgms. of residue after volatilisation and slight ignition of 50 gms. These traces of residue are usually present in other strong acids.

Sulphuric Acid.—2 gms. are evaporated to dryness in a platinum capsule on the water bath, and the capsule washed out with 50 c.c. of water; then 5 c.c. of hydrochloric acid (1 : 124) and 1 c.c. of barium chloride solution are added; no precipitate ought to appear within 5 minutes.

Arsenic, Heavy Metals, Earths, etc.—10 gms. are diluted to 40 c.c. with water. The solution is then heated and H_2S passed. No yellow or dark-coloured precipitate should appear (arsenic, or heavy metals). 5 gms. are diluted with 50 c.c. of water. After successive additions of ammonia (in excess), ammonium sulphide, ammonium carbonate, and ammonium phosphate, no turbidity should appear.

Silicofluoric and Hydrochloric Acids.—See under 'Quantitative Estimation". The permanganate test is described under "Uses".

Quantitative Estimation.—Hydrofluoric acid in aqueous solution may be estimated by normal alkali. When hydrofluoric acid and sulphuric acid are both present in the same solution the total acidity is first determined in one portion and the sulphuric acid is then estimated gravimetrically in another, the HF present being estimated by difference (Fresenius, "Anleitung zur quant. Analyse," 1875, vol. i., p. 643; also a method by W. B. Giles, described in Sutton, "Vol. Anal.," 7th ed., p. 106).

The estimation of silicofluoric in hydrofluoric acid depends upon the insolubility of potassium silicofluoride in cold water, and the precipitation may be effected by means of a sufficient quantity of a potash salt. The usual method is as follows: Potassium chloride and alcohol are added to the diluted acid and the precipitate of potassium silicofluoride washed with dilute alcohol, dried at 100°, and weighed. The alcohol must be added very carefully, and in not too large quantities at a time, otherwise precipitation of potassium chloride or fluoride is apt to ensue. For a rough estimate of the silicofluoric acid present it suffices to precipitate with potassium chloride in a cold, aqueous solution. For further details, see Fresenius, "Anleitung zur qual. chem. Analyse," 6th ed., pp. 400, 431. For the accurate determination of chlorine, fluorine, silicic acid, etc., see under "Sodium Fluoride".

Uses and Storage.—Hydrofluoric acid is used for the solution of insoluble silicates, and has recently been employed in the fermentation industry for the production of a purer ferment and a larger yield. The acid and its salts, even in very dilute solution, destroy lactic acid bacteria, but have no effect upon yeast. It is very poisonous.

Regarding the impurities produced through storage in vulcanite bottles, W. Hampe ("J.S.C.I.," 1891, p. 484) remarks that chemically pure hydrofluoric acid, after keeping for some time in the usual vulcanite bottles, decolorises permanganate, owing to absorption of organic substances—a fact which must be taken into account in employing the acid in the estimation

of ferrous oxide in silicates. Alkali is another impurity from the same source, rendering the acid which contains it useless for the analysis of silicates. Hampe states that the acid ought to be manufactured and stored in platinum bottles. According to R. Benedikt ("Analyst," 1891, p. 180) bottles made of pure vulcanite are well adapted for keeping the acid used for analytical purposes, but, if ordinary gutta-percha is used, the acid, after a short time, leaves a considerable residue on ignition, principally consisting of ferric oxide. A sample after being kept for a long time in pure vulcanite gave only 0·0005 gm. residue, using 25 c.c. of the acid. Heräus and Friedheim ("Zeit. f. angew. Chem.," 1895, p. 434) have also found the acid on long keeping to become impure and useless for many analytical purposes. Friedheim has repeatedly observed that commercial vulcanite is strongly adulterated with mineral substances. When the acid is kept in caoutchouc bottles it easily assumes a yellow appearance, and portions of the bottle itself may even be found in the liquid. As a rule, however, the impurities are so slight that no notice need be taken of them. It has been recommended also to use bottles of white cerasin.

Commercial Varieties.—An acid used for technical purposes may also be had, containing arsenic, silicofluoric, and sulphuric acids. Among the more recent literature on the subject, see Zellner, "Zeit. f. anal. Chem.," 1899; Eckelt, "Zeit. f. agnew. Chem.," 1899; and Stahl, "J.S.C.I.," 1896, p. 617.

HYDROFLUOSILICIC ACID.—Acid. hydrosilicio-fluoric. puriss. (SiF_6H_2). Mol. wt., 144·32. The solution in water is a clear, colourless liquid. Sp. gr., 1·06 containing about 7 per cent. of the acid.

Tests for Impurities.—*Residue.*—5 gms. must volatilise completely on heating in a platinum capsule.

Metals, etc.—(*a*) 5 gms. are diluted with 20 c.c. of water containing a little hydrochloric acid and hydrogen sulphide is passed; no coloration or precipitate must appear.

(*b*) On adding a solution of strontium nitrate (free from barium) to 5 gms. diluted with 10 c.c. of water, no turbidity should appear, even after long standing.

Quantitative Estimation.—The percentage may be estimated by titration with normal caustic soda, using phenolphthalein

or litmus as indicator; 6 molecules of soda are equivalent to 1 molecule hydrofluosilicic acid. Fresenius ("J.C.S.," 1890, A., p. 926) used 30·86 c.c. semi-normal caustic soda in titrating 10 gms. of an acid which he employed as a reagent, with phenolphthalein as indicator. 100 gms, therefore, contained 3·70 gms. hydrofluosilicic acid—

$$SiF_4(HF)_2 + 6NaOH = 6NaF + SiO_2 + 4H_2O;$$

1 c.c. normal alkali equals 0·02405 gm. SiF_6H_2. The following table gives the specific gravity, with percentage of acid present:—

Sp. Gr. of Hydrofluosilicic Acid and Percentage of H_2SiF_6 at 17·5° (Stolba).

Sp. Gr.	H_2SiF_6. Per Cent.	Sp. Gr.	H_2SiF_6. Per Cent.	Sp. Gr.	H_2SiF_6. Per cent.	Sp. Gr.	H_2SiF_6. Per cent.
1·3162	34·0	1·2285	25·5	1·1466	17·0	1·0704	8·5
1·3109	33·5	1·2235	25·0	1·1419	16·5	1·0661	8·0
1·3056	33·0	1·2186	24·5	1·1373	16·0	1·0618	7·5
1·3003	32·5	1·2136	24·0	1·1327	15·5	1·0576	7·0
1·2951	32·0	1·2087	23·5	1·1281	15·0	1·0533	6·5
1·2898	31·5	1·2038	23·0	1·1236	14·5	1·0491	6·0
1·2846	31·0	1·1989	22·5	1·1190	14·0	1·0449	5·5
1·2794	30·5	1·1941	22·0	1·1145	13·5	1·0407	5·0
1·2742	30·0	1·1892	21·5	1·1100	13·0	1·0366	4·5
1·2691	29·5	1·1844	21·0	1·1055	12·5	1·0324	4·0
1·2639	29·0	1·1766	20·5	1·1011	12·0	1·0283	3·5
1·2588	28·5	1·1748	20·0	1·0966	11·5	1·0242	3·0
1·2537	28·0	1·1701	19·5	1·0922	11·0	1·0201	2·5
1·2486	27·5	1·1653	19·0	1·0878	10·5	1·0161	2·0
1·2436	27·0	1·1606	18·5	1·0834	10·0	1·0120	1·5
1·2385	26·5	1·1559	18·0	1·0791	9·5	1·0080	1·0
1·2335	26·0	1·1512	17·5	1·0747	9·0	1·0040	0·5

Uses.—The acid is used for the separation of lime and baryta ("J.C.S.," 1891, A., pp. 500, 1552; 1892; A., p. 100).

Commercial Varieties.—These vary greatly with regard both to specific gravity and composition.

HYDROGEN PEROXIDE.—Hydrogen. peroxydat. puriss. (H_2O_2). Mol. wt., 34·01. A clear, transparent and slightly acid liquid, containing about 3 per cent. by weight of hydrogen peroxide, and strongly effervescing on addition of permanganate solution, the colour of the latter being discharged.

Tests for Impurities.—*Sulphuric Acid.*—10 c.c. are diluted

with 50 c.c. of water, a little hydrochloric acid is added and the mixture heated to boiling; on adding a few c.cm. of barium chloride solution no reaction must take place after standing for a few hours.

Alumina, etc.—10 c.c. are diluted with water, and ammonia and ammonium carbonate added; at most only a slight turbidity is allowed.

Phosphoric Acid.—5 c.c. are diluted with water, and a few c.cm. of magnesia mixture added, with excess of ammonia: only a slight turbidity should appear.

Magnesia.—5 c.c. are mixed with ammonia and a few c.cm. of sodium phosphate solution; only a slight turbidity should appear.

For further tests see under "Uses and Quantitative Estimation," also the following note.

Free Acid.—It must contain very little free acid; only a few tenths of a c.c. normal alkali should be used in neutralising 10 c.c. of a sample.

Note.—It may be remarked that Jannasch and Cloedt ("Zeit. f. anorg. Chem.," 1895, Nos. 5 and 6, p. 403; see also "J.C.S.," 1896, A., ii., p. 220) have obtained a preparation, by fractional distillation under reduced pressure, and subsequent separation by digestion with ether, which left absolutely no residue on evaporation. They employ this for the quantitative separation of the metals, which demands a specially pure reagent. For most analytical purposes the preparation described here is quite good enough, and leaves but a slight residue on evaporation.

Quantitative Estimation.—Criticisms on the various methods have appeared by such authors as Thoms and Gutzeit ("J.S.C.I.," 1887, p. 564), and Lunge (estimation by the nitrometer, "J.S.C.I.," 1885, p. 495) A detailed description of the nitrometer method is given in Winkler's "Gas Analysis," p. 106.

An easy and practical method is as follows: the hydrogen peroxide is titrated with a permanganate solution which has been previously standardised against oxalic acid, or a solution prepared directly from the purest potassium permanganate.

This method affords an approximate estimation. Decinormal permanganate is added to a solution containing 5 c.c. hydrogen peroxide in 50 c.c. of water and 10 c.c. of dilute sulphuric acid (1 : 4), until the pink colour remains permanent. One part of potassium permanganate is equivalent to 0·538

part of hydrogen peroxide. The compound is often sold as containing, e.g., 10 volumes of oxygen, instead of a guaranteed percentage of the substance itself. This means that the solution contains ten times its volume of oxygen, or 3·04 per cent. by weight of hydrogen peroxide.

Uses and Storage.—Classen and Bauer ("J.C.S.," 1883, A., p. 934) were the first to recommend its use as an oxidising agent for analytical purposes, particularly for the estimation of sulphur in hydrogen sulphide, metallic sulphides, and sulphurous and hyposulphurous acids. For such estimations, the substance must be absolutely free from sulphuric acid and generally answer all the tests given. These authors also use it for the estimation of hydrochloric and hydriodic acids in presence of hydrogen sulphide, in which case there must be no trace of the former acid present. The commercial article always contains a small quantity of either sulphuric or hydrochloric acid, intentionally added to preserve it, a fact which must not be disregarded. The hydrogen peroxide puriss., free from HCl, has to be prepared with sulphuric acid, and that used for sulphur estimations, with hydrochloric acid, but otherwise they are alike with regard to purity. Wilfarth employs the reagent for nitric acid estimations ("J.S.C.I.," 1888, p. 692), and calls particular attention to the fact that some commercial samples contain so much phosphate, etc., that a slimy precipitate is formed on adding caustic soda. Hanofsky ("Chem.-Ztg.," 1889, p. 99; see also "J.S.C.I.," 1885, p. 553) employs the peroxide in estimating the metals of the iron group. The "Pharm. Rundschau," 1893, p. 156, has an article on hydrogen peroxide. Baumann has based several gasometric methods on its action on chromic acid ("J.C.S.," 1892, A., pp. 103, 538). It may be used as a test for molybdic acid with which it gives a blood-red colour due to the formation of a permolybdate (P. Melikow, Merck's "Annual," 1912, p. 315). It can be concentrated to 50 per cent. or even more by distilling off the water *in vacuo* ("Pharm. Ztg.," 1894, p. 778).[1]

[1] The firm of E. Merck prepares a solution of pure hydrogen peroxide containing 30 per cent. by weight H_2O_2, sp. gr. about 1·111 at 15° C. under the name of perhydrol. Still more recently ("J.S.C.I.," 1902, p. 986) a solution containing 95-96 per cent. has been obtained. The H_2O_2 can be crystallised out, the chemically pure crystals melting again at − 2° C.

In the "Pharm. Ztg.," 1888, p. 20, mention is made of the fact that up to that time all commercial samples had been found to contain phosphoric acid and alumina. Scholvien also found nitric acid in the same qualities. According to Mann ("Chem.-Ztg.," 1889, p. 1377) these samples contain magnesium chloride. As the commercial quality, as well as that for medicinal purposes, is unfit for analytical work it is advisable that the purest only should be used. The commercial product is pure enough for the preparation of oxygen by the aid of bleaching powder or permanganate ("Rep. d. Chem.-Ztg.," 1889, p. 253). The solution, especially if no acid is added, readily decomposes on keeping, and ought therefore to be tested from time to time. Explosions have been known to occur owing to this decomposition, and as the action is assisted by the alkali present in the glass bottles it is advisable to add a few drops of hydrochloric or sulphuric acid.

The solution should be stored in glass bottles, and kept in a cool place. See also papers on "Hydrogen Peroxide" in "J.S.C.I.," 1890.

Note.—Sodium peroxide and barium peroxide are also used in analysis, the former extensively. Sodium peroxide is said to be preferable, when heated to redness, to all other oxidising agents ("Zeit. f. anorg. Chem.," 1892, p. 193). Poleck ("Chem.-Ztg.," 1894, p. 103; also "J.S.C.I.," 1894, p. 909) calls particular attention to its powerful action. It gives a copious evolution of oxygen on adding water, and, on mixing with powdered charcoal and gently heating, it ignites wood shavings. It oxidises iodine to periodic acid, reduces permanganate, and converts the metallic sulphides into sulphates. It is obtained as a pure white substance on burning sodium in dry oxygen, and sometimes contains particles of the metal. Fischer and Frost ("Ber. d. d. chem. Ges.," 1893, p. 3083) mention finding a jar of sodium peroxide containing a quantity of sodium. When thrown into water it dissolves with a hissing sound and slight ignition, and has been known to explode and shatter the vessel in this way. Regarding its use in analysis, see "Zeit. f. anal. Chem.," 1895, p. 593 *et seq.*; "Proc. Chem. Soc.," 1893, p. 184; and "J.S.C.I.," 1893, p. 868; 1895, p. 771.

Barium peroxide has been recommended by E. Donath for rendering some substance soluble through ignition, and that author also gives a detailed article on the use of barium and hydrogen peroxide in "J.C.S.," 1892, A., p. 1031. The substance may be obtained in the market, the commercial quality containing about 85 per cent. The pure substance is sold in both the hydrated and anhydrous forms.

Commercial Varieties.—See under "Uses and Quantitative Estimation". Commercial hydrogen peroxide solution contains sulphuric, hydrochloric, and nitric acids, as well as arsenic, phosphoric, silicofluoric and hydrofluoric acids, barytes, lime, alumina, and magnesia.

HYDROXYLAMINE HYDROCHLORIDE. — Hydroxylamin muriat. pur. : hydroxylamine hydrochloride (NH_2OH . HCl). Mol. wt., 69·50. Colourless crystals, easily soluble in water and alcohol.

Tests for Impurities.—*Ammonium Chloride.*—The alcoholic solution must give no precipitate with platinum bichloride.

Sulphuric Acid.—The aqueous solution must give no precipitate with barium chloride.

Residue.—The product must volatilise completely on ignition.

Quantitative Estimation.—The salt may be estimated by Fehling's solution and by other methods (Graham-Otto's "Lehrbuch der Chemie," 5th ed., vol. ii., p. 128). A solution of the salt is added drop by drop to boiling Fehling's solution; two molecules of cuprous oxide correspond to one molecule of hydroxylamine. Hydroxylamine heated with sodium nitroprusside and a trace of NaHO yields a magenta coloration. This reaction may be used as a colorimetric method of estimation (H. Schroeder, "Chem. News," 1914, pp. 109, 205).

Uses.—The salt is used in organic synthesis and in inorganic analysis. Its strong reducing property renders it serviceable in the precipitation of gold and silver. A method for the quantitative estimation of gold and silver by hydroxylamine hydrochloride is given by Leiner ("J.S.C.I.," 1892, pp. 271, 710).

Commercial Varieties.—The author has often found the salt to contain ammonium chloride. Recently the preparation has been brought into the market in a very pure state.

INDICATORS AND TEST PAPERS.—The more important indicators and test papers have been treated of under their special headings, as "Azolitmin," p. 43; "Cochineal Indicator," p. 72; "Congo Paper," p. 87; "Turmeric Paper," p. 339; "Haematoxyline," p. 118; and, later, litmus, lacmoid, methyl

orange, and phenolphthalein are similarly described. It may be remarked that, as a general rule, the depth of colour in the papers should be the same throughout, since with increase of colouring matter, the sensitiveness diminishes, and vice versa; the paper employed must also be neutral. It must also be remembered, when testing the sensitiveness, that some test papers quickly deteriorate. On the sensitiveness of indicators, see Lunge and Marmier, "Zeit. f. angew. Chem.," 1897, p. 3.

Comparative results regarding keeping qualities and sensitiveness are given below. With reference to the use of indicators in the volumetric estimation of alkaloids, see O. Linde, "Arch. d. Pharm.," 1900, vol. 238, p. 121 *et seq.*

1.—Table giving the results of comparative tests for sensitiveness of those indicators most generally employed.

The following table compiled by H. Trommsdorff was published for the first time in Böckmann, Chem.-techn. Untersuchungsmethoden, 3rd ed.; see also Cohn, "Indicators and Test Papers," p. 220.

Indicator.	Strength of Solution.	No. of c.c. Indicator Solution Added to 100 c.c. Water.	No. of c.c. Titrating Solution Employed to Produce Change in Colour.
Phenolphthalein	1 : 100 alcohol .	0·5	0·5 c.c. $\frac{n}{100}$ KOH used to produce a distinct red colour.
Methyl orange .	1 : 200 water .	0·05 0·10 0·20	1 c.c. $\frac{n}{100}$ HCl, titrated back with 0·9 c.c. $\frac{n}{100}$ NH_3 again acidified with 1 c.c. $\frac{n}{100}$ HCl, then 1 c.c. $\frac{n}{100}$ alkali added. The amount of indicator used appeared to be of no importance.
Ethyl orange .	1 : 400 (30 per cent. spirits of wine)	0·2	3 c.c. $\frac{n}{10}$ HCl. Evidently far less sensitive.
Tropaeolin 00 .	1 : 400 (30 per cent. spirits of wine)	0·2	2·5 c.c. $\frac{n}{10}$ HCl.

Indicator.	Strength of Solution.	No. of c.c. Indicator Solution Added to 100 c.c. Water.	No. of c.c. Titrating Solution Employed to Produce Change in Colour.
Phenacetolin .	1 : 200 alcohol .	{0·1 {0·2	0·1 c.c. $\frac{n}{10}$ KOH; with 0·2 c.c. change of colour more distinct.
Poirrier's blue .	1 : 200 water .	0·1	Titrated hot, 0·7 c.c. $\frac{n}{100}$ KOH, colourless, back to violet with 1·2 c.c. $\frac{n}{100}$ HCl.
Galleïn . .	1 part commercial product and 2 parts alcohol	0·1	1·2 c.c. $\frac{n}{100}$ HCl brownish, slightly bleached. 1·6 c.c. $\frac{n}{100}$ NH_3 violet, 1·2 c.c. $\frac{n}{100}$ HCl added, titrated back with 0·7 c.c. $\frac{n}{100}$ KOH.
Fluoresceïn .	1 : 100 alcohol .	0·1	Fluorescence disappeared with 0·5 c.c. $\frac{n}{10}$ HCl.
Litmus (purified)	1 : 10 water . .	0·2	0·05 c.c. $\frac{n}{10}$ HCl and 0·1 c.c. $\frac{n}{10}$ KOH respectively.
Azolitmin . .	1 : 100 water .	0·5	1·2 c.c. $\frac{n}{100}$ HCl and 3 c.c. $\frac{n}{100}$ KOH.
Orange-peel tincture .	1 : 5 water . .	1·0	0·1 c.c. $\frac{n}{10}$ KOH.
Congo red . .	1 : 100 (30 per cent. spirits of wine)	0·1	0·7 c.c. $\frac{n}{100}$ HCl and 0·6 ,, ,, NH_3; but 2·5 ,, ,, KOH.
Rosolic acid .	1 : 100 (60 per cent. spirits of wine)	0·5	0·7 c.c. $\frac{n}{100}$ HCl. 0·8 ,, ,, NH_3. 4·1 ,, ,, KOH.
Corallin . .	1 : 100 water .	0·5	0·6 c.c. $\frac{n}{100}$ HCl. 0·8 ,, ,, NH_3. 2·8 ,, ,, NaOH.
Carminic acid .	1 : 100 water .	0·5	0·7 c.c. $\frac{n}{100}$ HCl. 0·8 ,, ,, NH_3. 1·2 ,, ,, NaOH.
Cochineal . .	1 : 80 water . .	0·5	3·0 c.c. $\frac{n}{100}$ HCl. 2·8 ,, ,, NaOH.

For the above experiments 100 c.c. of distilled water were taken and a little of the colouring matter added; the standard solution was then added until a decided change of colour took place. When titrating with acid the solution was generally titrated back with a base, and then again with acid, and a different base used for bringing back, so that, as a rule, the action of the indicator towards acid, fixed alkali, and ammonia was observed.

2.—Table giving the limits of sensitiveness of test papers. Dieterich, "Pharm. Centralhalle," 1887, p. 498 (Cohn, p. 224).

Composition of Test Paper.	Parts of Water Employed for Dilution.			
Reaction Towards—	SO_3.	HCl.	KOH.	NH_3.
Blue litmus	40,000	50,000	—	—
Red litmus	—	—	20,000	60,000
Turmeric	—	—	18,000	35,000
Red alkannin	—	—	25,000	80,000
Blue alkannin	60,000	80,000	—	—
Logwood	—	—	35,000	90,000
Brazil wood	—	—	30,000	80,000
Dahlia	8,000	10,000	8,000	20,000
Bilberry	—	—	6,000	15,000
Elderberry	—	—	5,000	10,000
Buckthornberry	—	—	15,000	35,000
Cochineal	8,000	10,000	—	—
Rhubarb	—	—	8,000	20,000
Onion skin	—	—	8,000	20,000
Phenolphthalein	—	—	20,000	—
Tropaeolin	10,000	15,000	—	—
Rosolic acid	—	—	20,000	90,000
Congo red	2,500	3,000	—	—

According to Dieterich's results, alkannin paper must be recognised as being very sensitive, but it loses its valuable properties after a few days. Very sensitive logwood paper is affected in the same way. Congo paper has only a small degree of sensitiveness, but litmus and turmeric are as yet unexcelled, both with regard to delicate reaction and keeping properties.

3.—Table giving the sensitiveness of several test papers for the recognition of metals :—

	Iron as Fe_2Cl_6.	Copper as $CuSO_4$, $5H_2O$.	Iron as $FeSO_4$, $7H_2O$.	Lead as $Pb(C_2H_3O_2)_2$ $3H_2O$.	Bismuth as $Bi(NO_3)_3$ $5H_2O$.	Silver as $AgNO_3$.	Mercury as $HgCl_2$.
Potassium ferrocyanide .							
(1) on filter paper .	2,500	2,000	—	—	—	—	—
(2) on note paper .	1,000	300	—	—	—	—	—
Potassium ferricyanide .							
(1) on filter paper .	—	—	40,000	—	—	—	—
(2) on note paper . .	—	—	15,000	—	—	—	—
Potassium sulphocyanide							
(1) on filter paper . .	5,000	—	—	—	—	—	—
(2) on note paper . .	5,000	—	—	—	—	—	—
Potassium iodide . .							
(1) on filter paper .	—	—	—	500	7,000	1,000	—
(2) on note paper . .	—	—	—	—	100	100	—
Potassium chromate .							
(1) on filter paper .	—	—	—	2,000	—	3,000	—
(2) on note paper . .	—	—	—	50	—	50	—
Zinc sulphide							
(1) on filter paper .	—	15,000	—	15,000	7,000	8,000	1,200
(2) on note paper . .	—	15,000	—	15,000	3,000	8,000	1,200

In determining the limit of sensitiveness of starch paper, Dieterich takes a solution of 1 part iodine in 25,000 parts of water as his standard, and for the potassium-iodide-starch paper, 1 part of chlorine in 30,000 parts of water. To prepare the potassium ferrocyanide and other papers, filter paper is saturated with a solution (1 : 250) of the respective salt, or, in the case of notepaper, the solution is brushed over the paper. For the preparation of zinc sulphide paper, see loc. cit. Such papers are tested as follows: The filter paper preparation is dipped for 1 or 2 seconds into the solution of the salt to be tested and the change of colour noted. The paper made with ordinary notepaper is tested by touching it with 1 or 2 drops of the solution and noting the colour after 1 or 2 seconds have elapsed.

With regard to the newer indicators the following papers may be consulted: H. T. Tizard ("Proc. Chem. Soc.," 1910, 26, 225); M. T. Bogert and G. Scratchard ("J. Amer. Chem.

	Colour Changes.			P_H^+.
	Acid.	Neutral.	Alkaline.	
2-5-Dinitro-quinol	green	red-brown	purple	3-9·5
Di-o-hydroxystyryl ketone (lygosin)	brown-yellow	green	—	7·3-8·7
a-Naphtholphthalein	red	nearly colourless	blue	7·26-8·68
1-Oxynaphthochinomethane	—	colourless	purple	—
6-Sulpho-a-naphthol-1-azo-m-hydroxybenzoic acid	orange	blue	violet	7-12
6-Sulpho-β-naphtholazo-m-hydroxybenzoic acid	red	—	purple	—
2-6-Dinitro-aminophenol (isopicramic acid)	pink	—	yellow	4·1-5·6
Alizarinmonosulphonic acid	yellow	—	pink	3·7-4·2
Extract of red cabbage	red	blue	green	2·0-4·5
Diethyl red	,,	—	yellow	4·5-6·5
Dipropyl red	,,	—	,,	4·5-6·5
Dimethyl-a-naphthylamine red	purple	—	,,	4·5-6·5
Phenol-sulphone-phthalein (phenol red)	red-violet	—	,,	6·5-8·5
o-Cresol-sulphone-phthalein (cresol red)	,, ,,	—	,,	7·2-8·8
Thymol-sulphone-phthalein (thymol blue)	red	yellow	blue	1·2-9·6
a-Naphthol-sulphone-phthalein	blue	—	yellow	7·5-9·0
Tetrabromophenol-sulphone-phthalein (bromophenol blue)	purple	—	,,	2·8-4·6
Bromothymol-sulphone-phthalein	—	—	—	6·0-7·25
Methyl orange	red	orange	yellow	3-5
Methyl red	red	—	yellow	4·4-6·0
Dinitrobenzoyleneurea	colourless	—	green-yellow	6-8
Dibromo-o-cresol-sulphone phthalein (bromocresol purple)	yellow	—	purple	5·2-6·8
O-Carboxybenzene-azo-dipropylaniline (propyl red)	—	—	—	4·8-6·4
Dibromothymol-sulphone-phthalein (bromothymol blue)	—	—	—	6·0-7·6
O-Cresol-phthalein	—	—	—	8·2-9·8
Dibromo-o-cresol-sulphone phthalein (bromo-cresol purple	—	—	—	5·2-6·8

Soc.," 1916, 38, 1606-15; "J.S.C.I.," 1916, 945); H. A. Lubs and W. M. Clark ("J. Wash. Acad. Sci.," 1915, 5, 609-17; "J.S.C.I.," 1915, 1226; "J. Wash. Acad. Sci.," 1916, 6, 481-83 and 483-89; "J.S.C.I.," 1916, 980); F. Lehmann and G. Wolff ("Arch. Pharm.," 1917, 255, 113-19; "J.S.C.I.," 1917, 944); E. Rupp and R. Loose ("Ber.," 1908, 41, 3905-08; "J.S.C.I.," 1908, 1223); S. A. Kay and S. H. Newlands ("J.S.C.I.," 1916, 445); S. P. L. Sorensen and S. Palitzsch ("Compt. rend. Trav. Lab. Carlsburg," 1910, 9, 1-7; "J.S.C.I.," 1910, 1178) and R. Mellet ("Chem. Zeit.," 1910, 34, 1075). The useful range of the various indicators given on p. 145 are taken mostly from the papers of Lubs and Clark.

INDIGOTIN. — Indigotin. puriss. cryst.: indigo blue ($C_{16}H_{10}N_2O_2$). Mol. wt., 262·18. Small, bright copper red prisms, or deep blue powder, showing a coppery reflection and assuming a dark copper red colour on subjection to pressure. Sublimes at 300°.

Tests for Impurities.—*Residue.*—On igniting 1 gm. on platinum foil, the vapour must have a fine, purple-red colour, and only traces of residue must remain.

Quantitative Estimation.—See "Indigo," below.

Uses.—It is used in the preparation of the so-called "Indigo Solution," from indigotin. puriss. cryst. This solution is made by slowly dissolving 1 part of indigotin, in small quantities at a time, with constant stirring, in six parts of fuming sulphuric acid, and cooling to avoid rise in temperature. When all the indigotin has been added the vessel is covered, allowed to stand for 48 hours, and the contents poured into 100 times its volume of water; the solution is then mixed and filtered.

INDIGO.—Fine, dark blue lumps, showing a bronze streak when rubbed with the finger nail. For analytical purposes only the best Java indigo is used (see preparation of "Indigo Solution"; also under "Commercial Varieties").

Quantitative Estimation. — A really accurate, practical method for the valuation of commercial indigo does not at present exist. Among other methods, the following gravimetric process has been recommended (see Bolley, "Handbuch der chem-techn. Untersuchungen"): About 200 c.c. of hot

alcohol are poured over 5 gms. of the powdered indigo or indigotin, contained in an 800 c.c. stoppered flask; 7 gms. to 8 gms. of a syrupy solution of caustic soda (1·5 sp. gr.) are then added, and the flask completely filled with warm alcohol and stoppered. The solution is allowed to stand, with occasional shaking, for several days, till the liquid has completely settled. An aliquot portion is then syphoned off, and a current of air passed slowly through it until the indigo-white has separated as indigo-blue. The precipitate is filtered off, washed first with alcohol, then with dilute hydrochloric acid, and finally with water; it is then dried and weighed. Beilstein ("Handbuch d. organ. Chemie") considers that this method generally gives too low results, but none of the other methods which have been proposed for the assay of indigo (Mohr, "Titrirmethode," 6th ed., p. 800) are accurate, the results recorded being often too high. In indigo-carmine factories (see Wöscher, "J.S.C.I.," 1892, p. 428) a volumetric method by titration with $\frac{n}{10}$ permanganate is adopted, as follows: A good average sample is very finely powdered; 1 gm. is then weighed out and transferred to a 50 c.c. beaker, and 8 c.c. sulphuric acid containing 10 per cent. free SO_3 poured over it. The mixture is then heated, with constant stirring, to 50° or 60° on a sand bath. At the end of two or three hours the indigo has dissolved with formation of soluble sulphindigotic acid, the solution being then poured into a litre flask and made up to the mark. After shaking well 100 c.c. are drawn off into a porcelain basin, 400 c.c. water and 50 c.c. dilute sulphuric acid (1 : 10) added, and the solution titrated with permanganate. When the solution assumes an olive-green tint the permanganate is added cautiously, drop by drop, until a more or less orange-yellow colour appears. The number of c.c. are then read off: 1 c.c. $\frac{n}{10}$ permanganate = 0·007415 gm. indigotin. The results are satisfactory when the best samples are treated, as these do not usually contain foreign organic compounds which would interfere with the test.

Uses.—Indigo is used for the preparation of the ordinary indigo solution (see below), which is employed for the detection and estimation of nitric acid.

Commercial Varieties.—Java indigo ranks as the best of all

commercial varieties generally containing only the alumina compound, and seldom organic impurities. Wöscher records a sample containing 74 per cent. indigotin ("J.S.C.I.," 1892, p. 428). Bengal, Guatemala, and Chinese indigos are sometimes fairly good. In judging indigo from its external properties the chief point to observe is its degree of *softness;* the softer the sample and the more easily disintegrated, the higher is the percentage of the pure compound, as a general rule. As the impurities generally consist of lime salts, indigogluten, and other organic substances, in addition to sand and clay, these tend to bind and harden the mass. The best criterion of purity is presented by the estimation of the indigotin as described above, or the method by titration with $\frac{n}{10}$ permanganate.

INDIGO SOLUTION.—Solutio indici. An intensely blue liquid.

On the solution used in the Löwenthal-Schröder method for estimating tannin, see p. 149, and indigo solution from indigotin, see p. 146. The ordinary "solutio indici" is prepared from Java indigo; for 100 parts of solution, 2·5 parts indigo are taken and dissolved in fuming sulphuric acid as described on p. 146. This solution is prepared specially for the quantitative estimation of nitric acid, and is so standardised that 1 c.c. is equivalent to a certain quantity of nitric acid. Generally 1 gm. of the indigo is taken in 1 litre of water, the solution being then diluted until 5 c.c. give a bluish-green colour with 5 c.c. of a standard potassium nitrate solution (19·253 gms. KNO_3 per litre), to which 5 c.c. sulphuric acid have been added and heat applied. 5 c.c. of the indigo solution equals 60 mgms. HNO_3.

INDIGO-CARMINE. — Sulphindigotate of sodium, also called indigotin ($C_{16}H_8N_2O_2(NaSO_3)_2$). Mol. wt., 468·30. Indigo-carmine is obtained by precipitating the purified solution of indigo in sulphuric acid with common salt, and filtering; the pasty residue is indigo-carmine. Commercial "indigotin" is indigo-carmine in powder form, after having been more or less washed and dried.

Tests for Impurities.—According to Mierzinski (see Böck-

mann, " Chem.-techn. Untersuchungsmethoden," Berlin, 1893, and Allen's " Comm. Organ. Anal.," vol. iii., pt. i., p. 301) the quality of indigo-carmine may be tested by placing a very small quantity of the powder on unsized paper (filter paper); if the product is impure a greenish ring soon forms round the sample; this does not occur if the carmine has been well dried. To obtain a satisfactory result the sample should first be mixed with boiling water. For further qualities demanded of the pure product, see under " Uses ".

Quantitative Estimation.—Proceed as under " Indigo," p. 147.

Uses.—Indigo-carmine and indigotin are used in the preparation of standard solutions for the estimation of oxygen and particularly for the estimation of tannin by the Löwenthal-Schröder process. For the latter method, 30 gms. solid, air-dry sodium sulphindigotate are mixed with 3 litres dilute sulphuric acid (1 : 5, by vol.), and to this are added 3 litres of distilled water; the mixture is then shaken well till the carmine is dissolved; it is then filtered. Only the best indigotin or commercial indigo-carmine must be used. Neubauer and Schröder state that preparations are found which are perfectly useless for titration with permanganate, as at the end-reaction the greenish tint does not change to pure yellow, but a brown or reddish tint appears, thus rendering it impossible to tell when the oxidation is complete. It is necessary, therefore, to select an indigo which does not show this objectionable property in using the method described.[1] J. König also obtained varying results with different indigo-carmines in the estimation of oxygen in waters (" J.C.S.," 1892, A., p. 98). Indigo-carmine is also used for the preparation of this so-called " blue carmine paper," prepared by dipping very pure filter paper in an aqueous solution of indigo-carmine.

Commercial Varieties.—These differ considerably both with regard to purity and percentage of the pure salt. Girardin (" Lecons de chim. élément," 2, 618) arranges the carmines into three classes; he estimates the percentage of indigo-blue by permanganate and calculates to the compound carmine

[1] The Löwenthal-Schröder method is described in Böckmann, " Chem.-techn. Untersuchungsmethoden," 3rd ed., vol. ii., p. 518.

($C_{16}H_8(NaSO_3)_2N_2O_2$); three paste samples examined by him showed the following results:—

	$C_{16}H_8(NaSO_3)_2N_2O_2$, per Cent.	Water, per Cent.	Common Salt, per Cent.
Carmine 1 . .	5·41	76·66	17·93
Carmine 2 . .	8·56	84·80	6·64
Carmine 3 . .	10·14	85·17	4·69

IODINE. — Iodum resublimatum: iodine (I.). At. wt., 126·92. Blackish-brown rhombic scales with a metallic lustre, and absolutely dry; only very slightly soluble in water (1 : 5500), soluble in rectified spirits, ether, and chloroform; completely volatilised on heating.

Tests for Impurities.—*Appearance, etc.*—The crystals must be large, of uniform appearance, and dry; on being shaken up in a dry glass vessel, no particles must adhere to the sides.

Residue.—On carefully heating 1 gm. in a small porcelain crucible no residue must remain.

Cyanogen, Chlorine, and Bromine. — 0·5 gm. of the powdered sample is shaken up with 20 c.c. of water and filtered: on adding $\frac{n}{10}$ sodium thiosulphate to a portion of the filtrate till decolorised, and then a small crystal of ferrous sulphate, 1 drop of ferric chloride solution, and a little caustic soda solution, and finally applying gentle heat, the solution must not turn blue on adding hydrochloric acid in excess. The other portion of the filtrate after addition of ammonia in excess and precipitation with silver nitrate, must give a filtrate which shows only a slight turbidity after acidifying with nitric acid.

Note.—The foregoing test for chlorine and bromine (taken from the "Pharm. Germ.," iii.) seems to call for the observance of certain precautions, according to Salzer ("Pharm. Ztg.," 1891, p. 472). To about 10 c.c. of the aqueous solution are added 1 c.c. ammonia (sp. gr. 0·960), and 5 drops of silver nitrate (1 : 19), the mixture is then filtered and acidified; should too little ammonia be added the silver chloride which eventually forms would remain undissolved, and thus escape detection. For reference to the test for cyanogen, see Meineke, "J.S.C.I.," 1893, pp. 371, 550; "J.C.S.," 1893, A. ii., p. 246.

Bromine.—See below, under "Quantitative Estimation". Resublimed iodine must contain from 99 to 100 per cent.

Note.—According to Meineke ("J.S.C.I.," 1893, p. 550) the moisture may be estimated by covering the iodine with freshly ignited silver powder, and then igniting after combination has taken place. The remaining silver iodide is then weighed.

Quantitative Estimation.—The well-known method of dissolving a quantity of the sample in potassium iodide solution and titrating with $\frac{n}{10}$ sodium thiosulphate is the one generally used. 1 c.c. thiosulphate solution = 0·012692 gm. iodine.

In the quantitative analysis of resublimed iodine, the most practical method is to standardise the thiosulphate solution on iodine previously purified by Stas's process (drying over sulphuric acid and fusing).

Topf ("Zeit. f. anal. Chem.," 1887, p. 288 *et seq.*; and "J.C.S.," 1887, A., p. 997) estimates iodine in a commercial sample (containing chlorine) by dissolving the iodine in caustic soda solution, adding sodium bisulphite and ferric chloride, then excess of hydrochloric acid, and distilling till all the iodine has passed over into a solution of potassium iodide; the solution is then titrated with thiosulphate in the ordinary way. The process is described in detail in the above article by Topf. Topf's method is a modification of the original one by Duflos, according to which the iodine in iodides and hydriodic acid may be estimated indirectly, in presence of chlorine and bromine, by means of ferric chloride. This method is based on the fact that when a solution of an iodide or hydriodic acid is heated with ferric chloride, or, better still, with an acid solution of ferric sulphate, all the iodine is liberated and a ferrous salt is formed. Potassium bromide is not decomposed by ferric chloride, even at 100° (E. Schmidt). The distillation is carried on until no more violet vapours appear in the tube; the iodine is retained by potassium iodide and estimated in the usual way. For further details, see Topf, loc. cit. G. Weiss ("J.S.C.I.," 1885, p. 689) remarks on the large amount of bromine (3 per cent.) he found in a commercial sample of iodine. This author effects the separation of chlorine, bromine, and iodine by heating and passing a current of air through the substance in presence of a fairly concentrated solution of ferric sulphate, the iodine being retained by a concentrated solution of potassium iodide which he titrates with sodium thiosulphate. The residue

is cooled, potassium permanganate added, and heated to 50° or 60°, and again a current of air passed through, the liberated bromine being absorbed by ammonia and titrated. The chlorine is obtained by difference. The separation of chlorine, bromine and iodine is described in Fresenius, "Quant. Anal.," 7th ed., p. 509, and other textbooks; also in this work under "Potassium Iodide". When the halogens exist in the form of chlorides, bromides, and iodides, the gravimetric method with palladium gives good results. The iodine is precipitated with palladium monochloride from a solution slightly acidified with hydrochloric acid; the resulting palladium iodide is dried and weighed. When the chlorine has also to be estimated,[1] protoxide of palladium is employed. The palladium in the filtrate is removed by means of hydrogen sulphide, the latter driven off, and the chlorine, and subsequently the bromine, estimated with silver nitrate; hydrochloric acid must not, however, be used for acidifying. The precipitate of palladium monoiodide is allowed to settle for a day or two before filtering; it is then dried at 100°, at which temperature only a trace of iodine is lost. Palladium iodide is composed of 29·59 per cent. Pd, and 70·41 per cent. I. PdI_2 is insoluble in water and dilute hydrochloric acid, and remains unchanged in contact with the atmosphere.

Uses, Storage, and Deci-normal Iodine Solution.—Iodine is used in the preparation of standard iodine solutions, particularly the deci-normal solution, and is extensively employed for the numerous quantitative estimations of organic and inorganic compounds. It is used in microscopical investigations for the detection of starch, and in conjunction with sulphuric acid or zinc chloride, for the recognition of amyloid and cellulose; also in the practical testing of paper by the microscope (see Griffin and Little, "The Chemistry of Paper Making," p. 443, and "Rep. d. Chem.-Ztg.," 1889, p. 155), and is much used in organic synthesis. It must be kept in a cool place and closely sealed. According to Topf, its poor keeping qualities place it at a disadvantage as a standard, not because, as often

[1] According to E. Schmidt, palladium nitrate produces a precipitate in solution of bromide of potassium, but palladium monochloride does not.

stated, of its hygroscopic nature,[1] but on account of the difficulty in protecting it from the particles of dust which adhere to the stoppers, these forming with the sublimed iodine a brown sticky mass which soon finds its way into the bottle. Iodine solutions lose their strength on keeping, and on this account Topf, Thon, and Meineke all propose to use the neutral or acid iodate of potassium as a standard in iodometry (see "Potassium Iodate"). Fresenius ("Quant. Anal," vol. i., p. 371) states that the solution of iodine in potassium iodide, even when kept in a dark, cool place, suffers more deterioration than is commonly supposed, and recommends restandardising before use. Stas's method of standardising iodine and thiosulphate solutions by means of absolutely pure iodine is described by Fresenius (loc. cit.).

Iodine has been used by Bardach ("Med. Klinik," 1908, p. 1664; Merck's "Annual," 1910, p. 237) as a test for acetone in urine, with which it forms a turbidity due to iodoform.

Commercial Varieties.—In addition to the above described, raw commercial forms, known as English and French iodine, are to be found in the market. These varieties sometimes contain sand and moisture; even samples of sublimed iodine have been known to contain chlorine, bromine, and cyanogen. Raw English iodine is said to be purer than the French. Tissandier records analyses of raw iodine ranging between 76·21 and 94·12 per cent. iodine. The author during his investigations has found very pure English samples containing from 98 to 99 per cent., and even more. High results are often obtained on titrating commercial iodine with potassium thiosulphate—a fact which indicates the presence of chlorine and bromine. Meineke mentions having obtained 100·5 per cent. in an impure commercial sample; it is therefore necessary to use the method adopted by Topf or Weiss (see p. 15).

IODINE PURISS. for IODOMETRY.—This preparation must contain 99·98 to 100 per cent., and ought only to be sold with an accurate guarantee of its percentage or purity. It is

[1] Meineke proves that iodine, even when placed in contact with moist air for some time, only absorbs a very small quantity of moisture ("Chem.-Ztg.," 1892, p. 1121).

prepared either by the process recommended by Meineke or by Stas (for details as to the preparation and testing, see Meineke, loc. cit.). Iodine purified by either of the above-mentioned methods may be used as a standard in iodometry, and must be kept cool and well stoppered (see under "Iodine").

IODINE IN ZINC-CHLORIDE SOLUTION.—This is prepared by dissolving 100 gms. of zinc chloride, 20 gms. of potassium iodide, and 0·5 gm. of iodine in 60 c.c. of water.

Uses.—It is employed in the detection of cellulose in plant cells and in textiles. Cellulose immediately swells up in the liquid and is stained a deep blue.

IODINE TRICHLORIDE.—Iodum trichloratum (ICl_3). Mol. wt., 233·3. Lemon yellow crystals.

Tests for Impurities.—On gently heating it should leave no residue. It is entirely soluble in alcohol, ether, and glacial acetic acid.

Uses.—It is employed in the preparation of Wijs' solution for the determination of the iodine values of fats.

Solutions for Determining Iodine Value.—*Wijs' Solution.*—This solution is prepared by dissolving 7·9 gms. of iodine trichloride and 8·7 gms. of iodine separately in glacial acetic acid, mixing the two solutions and making up to 1 litre with glacial acetic acid.

As the acetic acid may contain formic acid, it should previously be tested by heating with potassium bichromate and sulphuric acid, which should not develop a green colour (see Lewkowitsch, "Technology of Oils, Fats, etc.," 1913, vol. i., p. 407).

Hubl's Solution.—Hubl's solution consists of: (1) 25 gms. of iodine dissolved in 500 c.c. of pure 95 per cent. alcohol; (2) 30 gms. of mercury bichloride dissolved in 500 c.c. of 95 per cent. alcohol. These two solutions are mixed in equal volumes and then allowed to stand 24 hours before using. (See Lewkowitsch, "Technology of Oils, Fats, etc.," 1913, vol. i., p. 396.)

Waller's Solution.—This is prepared by dissolving 25 gms. of iodine in 200 c.c. of strong alcohol. Another solution

is prepared by dissolving 25 gms. of mercuric chloride in 200 c.c. of strong alcohol, and adding 25 c.c. of strong hydrochloric acid, sp. gr. 1·19. These two solutions are then mixed and made up to 500 c.c. with alcohol (Lewkowitsch, "Technology of Oils and Fats, etc.," vol. i., p. 401).

Hanu's Solution.—13·2 gms. of iodine are dissolved in 1000 c.c. of glacial acetic acid. Add about 3 c.c. of bromine to the solution. The amount of bromine added should be sufficient to just double the halogen content, which is determined by titration.

Storage of Iodine Trichloride.—This compound readily decomposes in contact with air giving off chlorine. It should be stored in small, sealed tubes, which should be again sealed off after the portion to be used has been removed.

IODEOSIN (ERYTHROSIN), ($C_{20}H_8I_4O_5$).

The alkali salt of tetraiodo fluoresceïn. Mylius and Förster ("Berichte d. d. chem. Ges.," 1891, vol. xxiv., p. 1483), also Cohn ("Indicators and Test-papers," p. 93) recommend this indicator for the estimation of minute traces of alkali—e.g., such quantities as water would dissolve from glass. The commercial product is purified by dissolving in aqueous ether and shaking the filtered solution with dilute caustic soda. The sodium salt is precipitated from the alkaline solution with stronger caustic soda; the brick-red precipitate is washed with rectified spirit and recrystallised from hot alcohol. The aqueous solution from the sodium salt is now precipitated with hydrochloric acid and the precipitate thoroughly washed. The powder, dried at 120°, has the composition given above.

Iodeosin is only used for the detection of traces of alkali, such as are present in the instance quoted; the alkali is estimated with $\frac{n}{1000}$ solution. The titration may be performed with advantage in a small-stoppered bottle, to which from 10 to 20 c.c. of an ethereal solution of iodeosin are added, with 50 to 100 c.c. of the solution to be tested. The solution of the indicator must not contain more than 2 mgms. per litre of the powder. In the presence of free alkali the lower layer shows a pink colour on standing. For further details on the process, see loc. cit.

The author considers that for the titration of alkaloids the ordinary sodium salt of iodeosin as manufactured by the Badische Anilin und Sodafabrik serves the same purpose as the purified tetraiodofluoresceïn of Mylius and Förster. It may be mentioned that, under the name "iodeosin," not only do we find the pure tetraiodofluoresceïn, but also the potash and soda compounds, and also diiodofluoresceïn with its corresponding alkali compounds, which are likewise used as indicators in alkalimetry. Pure tetraiodofluoresceïn is soluble in ether but not in water (provided the water contains no traces of alkali), while the reverse holds with regard to the sodium and potassium salts. It is thus an easy matter to differentiate between the base itself and its alkali compound.

IODIC ACID.—Acid. iodicum pur. (IO_3H.). Mol. wt., 175·93. Colourless crystals, easily soluble in water but insoluble in ether and alcohol. Chlorine water and reducing substances liberate iodine from the acid.

Tests for Impurities.—*Residue.*—2 gms. must leave no weighable residue on ignition.

Solubility.—The acid must dissolve in water to a clear solution.

Quantitative Estimation.—For the estimation, 0·1 gm. of the iodic acid (or iodate of potassium) is dissolved in about 100 c.c. of water, potassium iodide added in excess, and some dilute sulphuric or hydrochloric acid; the iodine liberated is then estimated with $\frac{n}{10}$ thiosulphate, using starch solution towards the end as indicator (Sutton, "Vol. Anal.," 7th ed., p. 166).

Uses.—The aqueous solution of iodic acid forms a strong oxidising agent, and is used in organic synthesis. It is a characteristic reagent for morphine (Allen, "Comm. Org. Anal.," vol. iii., pt. ii., p. 318). On the use of iodic acid for standardising purposes, see C. F. Walker, "J.C.S.," 1898, A., ii., p. 44.

Commercial Varieties.—Iodic anhydride (I_2O_5) can also be obtained in the market.

IRIDIUM TETRACHLORIDE. — Iridium tetrachloride ($IrCl_4$). Mol. wt., 334·94. A brownish-black hygroscopic substance.

Uses.—It is recommended by Gustav Eisen ("Zeitschr. für Microskop.," 1897, vol. xiv., p. 193) as a particularly good fixing agent in microscopy.

IRON.—Ferrum (Fe). At. wt., 55·84. Iron is used either in the form of thin bright wire (iron wire) or as a grey powder, formed by reduction with hydrogen (Ferrum hydrogenio reductum); also in the form of ordinary bright-grey iron powder (Ferrum pulveratum).

1. **Iron Wire.**—Iron wire is used for ascertaining the strength of permanganate solutions (see Sutton's "Vol. Anal.," 7th ed., p. 122), and for this purpose a thin, soft wire (flower wire), containing about 0·4 per cent. carbon, is used.

Note.—If great accuracy is required in the above determination, an analysis of the wire must first be made; in this case the permanganate solution is first of all standardised on electrolytically deposited iron, after the method described by Classen (see W. Crookes, "Select Methods in Chemical Analysis," p. 161, and "J.S.C.I.," 1882, p. 236), and this permanganate solution is then used to determine the amount of iron present in the wire, or the impurities may be estimated (P, Si, C, and Mn) and the iron calculated by difference. In this way a good permanent means of standardising permanganate solutions is obtained, provided the analysis of the iron has been carefully and accurately conducted.

2. **Iron Powder, prepared by reduction with Hydrogen.**—A dull grey powder,[1] which must contain at least 90 per cent. metallic iron, and on solution in an acid must leave only 0·01 per cent. of residue. According to the Official German "Arzneibuch," a preparation passing the above tests is sufficiently pure for most analytical purposes, e.g., the estimation of nitric acid by the reduction method, where it is used in conjunction with zinc dust in place of the ordinary iron powder.

[1] The "Pharm. Germ. III." describes the above as a lustreless powder, but on this point I should like to remark that, from my own observations, ferrum hydrogen. reduct. prepared exclusively from pure iron oxide and hydrogen, on a large scale, always contains in greater or lesser degree particles presenting a bright surface. It is therefore wrong to assume that a powder such as this has been adulterated with ordinary iron powder; Glücksmann has evidently fallen into this error (see "Zeit. des allgem. österreich. Apotheker-Vereins," 1895, No. 36).

Note.—The test for arsenic is conducted in Marsh's apparatus, with the addition of zinc (Sauttermeister, "J.S.C.I.," 1891, p. 949). Without this addition of zinc any arsenic present would escape detection owing to its precipitation in the metallic state. The arsenic therefore remains as an insoluble residue in the acid after the iron is dissolved. The insoluble residue which is obtained on dissolving iron in hydrochloric acid should be tested for arsenic particularly. Reduced iron has also been advocated for the quantitative estimation of sulphur in insoluble sulphides (Treadwell, "J.S.C.I.," 1891, p. 951); for that purpose it must be perfectly free from sulphur. Tests for sulphur, see under "Zinc".

3. Iron Powder.—A heavy, bright, fine, metallic powder, containing about 98 per cent. metallic iron, and of a degree of purity sufficient for most analytical purposes, if made according to the specification of the above-mentioned "Arzneibuch". The quantitative estimation of the metal in this preparation, and the preceding one, is conducted in the same way as under "Zinc Dust," namely, by measuring the hydrogen evolved on addition of acid, and calculating the equivalent amount of metal. Regarding the method for the quantitative determination prescribed by the Third German Pharmacopœia, Seubert ("Arch. d. Pharm.," 1892, p. 142) affirms that the methods may readily cause inaccuracy. Finally, mention may be made of the copper-deposited iron powder, a form which has been recommended and adopted for the evolution of hydrogen in the estimation of nitric acid ("Chem. Industrie," 1892, p. 90).

IRON ALUM.—*Formula.*—$K_2SO_4,Fe_2(SO_4)_3 24H_2O$. Mol. wt., 1006·46. This is in the form of large yellowish-brown hexagonal crystals.

Uses.—It is employed as an indicator in Volhard's method of estimating chlorides, also for distinguishing the varieties of tannin.

IRON CHLORIDE (FERRIC).—Ferrum sesquichloratum (Fe_2Cl_6, $12H_2O$). Mol. wt., 540·63. Yellow crystalline mass, having a faint odour of hydrochloric acid; soluble in water, alcohol, and ether-alcohol.

Tests for Impurities.—The tests for this salt have been taken from the Third German Pharmacopœia, a solution con-

taining 1 part of iron chloride in 1 part of water being employed.

Hydrochloric Acid and Chlorine.—On approaching the solution with a glass rod moistened with ammonia, or a piece of paper dipped in zinc iodide and starch solution, there must appear neither white fumes nor a blue coloration on the paper.

Arsenic.—On adding 3 c.c. of stannous chloride solution to 1 c.c. of the solution to be tested, no coloration must take place within 1 hour.

Note.—Arsenic can also be detected by means of Marsh's test, but it is hardly possible to obtain a commercial arsenic-free ferric chloride which does not respond to this severe test. Buchner ("Chem.-Ztg.," 1887, p. 417, also "J.S.C.I.," 1887, p. 522) calls attention to the fact that commercial iron chloride solution often contains large quantities of arsenic. Great care must be observed in conducting Marsh's test, and Buchner makes the following observation on this point, loc. cit.: "Where very small traces of arsenic have to be detected, as for example in testing pure hydrochloric acid to be used for forensic purposes, I have known two chemists, using precisely the same materials, to obtain such discordant results that one declared the acid to be perfectly arsenic-free, while the other reported the presence of a considerable quantity. The reason for this diversity lay in the degree of heat applied to the reduction tube; while the one chemist, through not having gas in his laboratory, used a Berzelius spirit lamp, the other used the ordinary Bunsen. In the first instance no arsenic mirror was obtained even after passing the gas for hours through the faintly glowing tube, whereas in the tube heated by the Bunsen a faint arsenical mirror appeared after a few minutes.

"I have drawn attention to this case in order to point out that, in Marsh's test, special attention must be paid to the manner in which the reduction tube is heated, and to the temperature employed."

It may also be mentioned that glass often contains arsenic. Marshall and Potts ("Amer. Chem. Journ.," 1888, 10, p. 425) found the percentage of arsenious acid (As_2O_3) in laboratory vessels made from both German and Philadelphian glass to vary from 0·095 to 0·306 per cent. The reduction tube should be made of glass, free from lead, according to Otto (Ausmittelung der Gifte); he also condemns the use of red rubber tubing, as often containing sulphide of antimony. Arsenic is reported as having been detected in vulcanised rubber tubing.[1] In testing iron perchloride or hydrochloric acid, a coating sometimes appears in the tube, which is almost immediately oxidised to a white film in contact with air; this appearance is known as the

[1] Unger ("J.S.C.I.," 1885, p. 354) quotes an analysis of vulcanised rubber tubing.

zinc mirror, and is liable to mislead the operator; the arsenic mirror can always be recognised by its well-known reaction. It is therefore evident that unless every precaution is taken, Marsh's test may prove a fruitful source of error to the careless operator, and in testing iron perchloride, the simple test of the German Pharmacopœia is to be preferred.

Ferrous Chloride.—The preparation is diluted with 10 parts of water and acidified with hydrochloric acid; addition of potassium ferricyanide solution must not produce a blue coloration.

Copper, Nitric Acid, and other Impurities.—5 c.c. of the concentrated solution on addition of 20 c.c. of water and excess of ammonia solution must give a colourless filtrate, and on evaporating this and igniting slightly no weighable residue must remain. If 2 c.c. of this filtrate are mixed with 2 c.c. sulphuric acid, and 1 c.c. of a solution of ferrous sulphate carefully added, no brown ring must appear at the point of contact. Another portion of this filtrate, on being acidified with acetic acid must exhibit no change on adding either barium nitrate or potassium ferrocyanide solution.

Quantitative Estimation.—The iron is usually precipitated with ammonia and weighed as oxide of iron, but the perchloride may also be estimated by titrating with sodium thiosulphate, after digestion with potassium iodide (see Sutton, "Vol. Anal.," 7th ed., p. 212).

Uses and Storage.—Iron perchloride is used for the detection of thiocyanic, ferrocyanic, salicylic, and tannic acids, and also in the preparation of organic acids and the decomposition of the phosphates of the alkaline earths. The salt in solution ought to be kept in a dark place.

Commercial Varieties.—Samples containing arsenic and sulphuric acid are sometimes found in the market, and the freedom from or presence of nitric acid in the salt is recognised as a means of distinction in commerce.

IRON CHLORIDE (FERROUS). — Ferrum chloratum ($FeCl_2,4H_2O$). Mol. wt., 198·82. Bluish monoclinic crystals, which become green on exposure to air, hygroscopic, giving a green solution with its own weight of water and 1 drop of hydrochloric acid.

Tests for Impurities.—*Oxychloride.*—The above-mentioned solution must be green or pale green without showing any yellow tinge, and on admixture with several times its volume of hydrogen sulphide solution, only a slight turbidity must appear, due to the separation of sulphur.

Copper, Arsenic, Sulphuric Acid, etc.—These tests are conducted as under "Iron Perchloride," the iron being previously oxidised.

Quantitative Estimation.—The solution of the salt is titrated with decinormal permanganate solution.

Uses and Storage.—The salt is used in Schlösing's process for the determination of nitric acid. It must be preserved in well-stoppered glass vessels.

Commercial Varieties.—These often contain considerable quantities of oxychloride, arsenic, and sulphuric acid.

IRON AMMONIUM SULPHATE.—Ferro-ammon. sulphuric. puriss. cryst. $((SO_4)_2Fe(NH_4)_2, 6H_2O)$. Mol. wt., 392·14. Bluish-green crystalline powder (monoclinic) containing approximately one-seventh of its weight of iron. Soluble in water (1 : 5).

Tests for Impurities.—*Oxide.*—A 5 per cent. solution of the salt in water which has been thoroughly boiled and cooled again out of access of air ought only to show a slight red colour on adding potassium thiocyanate. The quantitative estimation also indicates the quality of the salt in this respect.

Note.—For preparing a standard solution, the salt must be carefully dried, and must contain 100 per cent. of the compound. The commercial salt generally develops small traces of oxide on keeping.

Quantitative Estimation.—A permanganate solution is first prepared in the usual way (3·2 gms. $K_2Mn_2O_8$ per litre), and standardised on flower wire, free from rust (see Sutton, "Vol. Anal.," 7th ed., p. 122). The wire[1] is dissolved in sulphuric acid in a flask with a rubber valve, the air being carefully excluded.

[1] It must be mentioned that flower wire generally contains impurities to the extent of 0·4 per cent., consisting of carbon, manganese, and copper, therefore 1 gm. of the wire would correspond to only 0·996 gm. pure iron. Classen takes pure iron prepared by electrolysis instead of the former. See under "Iron," p. 157.

The estimation of the iron salt is conducted as follows: 0·7 gm. is dissolved in 50 c.c. of water acidified with a little sulphuric acid, and the permanganate solution added until a red colour is produced; the quantity of iron equivalent to 1 c.c. of permanganate solution being known, it is easy to calculate, from the number of c.c. used, the true composition of the double salt. 0·7 part double salt must be practically equivalent to 0·1 part metallic iron. Another method is to titrate separately 1 part of iron and 7 parts of the double salt, using the same permanganate solution. The same number of c.c. should be used in both cases if the salt has the right composition.

Uses and Storage.—Ferrous ammonium sulphate, also called "iron double salt," is particularly recommended by Mohr for the titration of permanganate solution. According to Pawolleck ("Ber. d. d. chem. Ges.," xvi., p. 3008) not only does the salt keep well, but its decinormal solution is also fairly stable. Classen, on the other hand, emphasises the point that, owing to the facility offered by the crystals for retaining minute quantities of water, the salt cannot be recommended for standardising purposes. Against this, Mohr prepares his salt in the form of a powder, thus considerably reducing the risk of hygroscopical water being present. According to him, the salt prepared from pure materials, stirred during crystallisation, is freed from the mother liquor by means of the centrifugal; it is finally dried on filter paper in a moderately warm place until the crystalline powder has almost the appearance of fine grain sporting powder. The carefully dried salt is preserved in well-stoppered bottles.

Commercial Varieties.—The salt can either be obtained as ferrous ammonium sulphate, pure for analysis, or in the form of large crystals.

IRON SULPHATE.—Ferrum sulphuric. puriss. Ferrous sulphate. cryst. ($FeSO_4, 7H_2O$). Mol. wt., 277·93. Bluish-green crystals or crystalline powder, giving a perfectly clear solution with water (1 : 1·4) which has been thoroughly boiled.

Tests for Impurities.—*Copper, Zinc, etc.*—2 gms. are dissolved in water, oxidised by boiling with a little nitric and

hydrochloric acids, the iron precipitated with excess of ammonia, and the solution filtered. One portion of the filtrate must show no change on addition of ammonium sulphide; another portion, on addition of acetic acid in excess and potassium ferrocyanide, must not indicate the presence of copper.

Other Impurities.—5 gms. are dissolved in water, oxidised with nitric and hydrochloric acids and precipitated with ammonia as before; on evaporating the filtrate to dryness and igniting, only traces of residue must remain.

Free Acid and Solubility.—The solution (1 : 20) prepared with freshly boiled and cooled water, must be clear and of a greenish-blue colour, and must give almost no acid reaction with blue litmus paper. It must contain at least 99 per cent. $Fe_2SO_4, 7H_2O$.

Note.—Although the salt may not contain any impurities it is not possible to guarantee 100 per cent., as, in the drying process, where large quantities are being treated, a small portion of the water of crystallisation escapes very readily. Considering that the salt is seldom used for the preparation of standard solutions, this is generally of no importance. Biltz ("Kritische Notizen zur Pharm. Germ.," Stenger, Erfurt, 1878) concludes from his observations that a preparation containing 99 per cent. may be demanded.

Quantitative Estimation.—To determine the percentage of the salt present, 1 gm. is dissolved in water which has been well boiled; dilute sulphuric acid is then added, and the solution titrated with $\frac{n}{10}$ permanganate till a faint pink colour remains; from the number of c.c. used the percentage of $FeSO_4, 7H_2O$ is calculated (Sutton, "Vol. Anal.," 7th ed., p. 207).

Uses and Storage.—Pure ferrous sulphate is used for the detection of nitric acid and cyanogen, the estimation of gold, etc., and particularly in the preparation of ferrous ammonium sulphate. If stored in well-closed glass vessels, it remains practically unchanged for years, according to Biltz (loc. cit.).

Commercial Varieties.—Green vitriol may be obtained both in the precipitated condition described above and also in the form of beautiful bluish-green crystals; but, according to Biltz (loc. cit.), the salt keeps better in the former condition. The principal impurity is oxide, the presence of which is at once seen from the appearance of the salt. The crystals must

not present a grass-green appearance, but must have a distinct blue tinge, and no yellow coating of the afore-mentioned oxide. The raw salt (copperas) often contains copper, manganese, zinc, and sometimes arsenic; a good sample of this variety must be fairly transparent, and of the appearance already described.

IRON SULPHIDE.—Ferrum sulphuratum, protosulphide of iron (FeS). Mol. wt., 87·90. Bright, heavy, metallic lumps, copiously evolving hydrogen sulphide on treatment with acids.

Tests for Impurities.—*Arsenic.*—The ferrous sulphide is decomposed with pure dilute sulphuric acid free from arsenic; the gas evolved is first washed and then passed into pure arsenic-free nitric acid, the latter being then subjected to Marsh's test.

Note.—Otto ("Ausmittelung der Gifte") examined several samples of ferrous sulphide by this method, and always found traces of arsenic. He, in conjunction with other investigators, considers it advisable to use barium or calcium sulphide for the preparation of arsenic-free H_2S. Several methods have been proposed for purifying H_2S prepared from monosulphide. Otto, "F. v. d. Pfordten" ("J.S.C.I.," 1885, p. 403) recommends passing the freshly evolved gas over heated potassium sulphide.

Quantitative Estimation.—The estimation of the sulphur in iron monosulphide is conducted, according to Mohr's "Titrirmethode," as follows: 0·5 gm. of the finely-powdered sample is dissolved in excess of strong hydrochloric acid, and the gas evolved passed through one or, preferably, two receivers containing standard iodine and a little starch solution. After decomposition is complete the excess of iodine solution is titrated with standard sodium thiosulphate, the quantity of iodine used representing the sulphur present. The iron in the generator exists as ferrous chloride, and may be estimated in the cold with standard permanganate. If the ferrous sulphide contains any disulphide the latter will remain undissolved.

Uses.—For the preparation of hydrogen sulphide.

Commercial Varieties.—The commercial sulphide generally contains less than one equivalent of sulphur. Mohr ("Lehrbuch der Titrirmethode," 6th ed., p. 722) analysed some samples and found 25·93 and 27·16 instead of 36·39 per cent. sulphur. The author, in testing samples from various sources, generally

found 26 to 28 per cent., and sometimes as low as 22 per cent. of available sulphur. The producers do not generally give a guaranteed percentage, owing to the difficulty in collecting a homogeneous sample from the various batches; notwithstanding this, 24 per cent. available sulphur may be demanded.

KNAPP'S SOLUTION. — Standard solution of mercuric cyanide used in the estimation and differentiation of the sugars.

This solution is prepared by dissolving 10 gms. of pure mercuric cyanide in 600 c.c. of distilled water. To this is added 100 c.c. of a solution of sodium hydroxide, sp. gr. 1·145, and the whole made up to 1000 c.c. with distilled water.

LACMOID AND DIAZORESORCIN.—1. Lacmoid,

$$C_6H_3(OH)_2 \cdot N \cdot C_6H_3O \cdot OH.$$

Dark blue-violet scales, soluble in alcohol, difficultly soluble in water.

Tests for Impurities.—According to Förster ("J.C.S.," 1891, A., p. 241), the degree of solubility is a most important matter, as it often happens that little or no blue colouring matter dissolves on treatment with water; it is better to abstain from using such samples. If, however, the sample imparts a fine blue colour to boiling water it may be used with advantage. The alcoholic solution must also have a fine blue colour with only a slight violet tinge. The purest lacmoid must exhibit the above properties in a marked degree, and its solution as an indicator must be sensitive. Förster tests the lacmoid solution by comparison with a similar litmus solution. He dissolves each compound in water free from CO_2 (see p. 177), preserving the same depth of colour, and acidifying by adding an equal number of drops $\frac{n}{5}$ sulphuric acid to both; he then brings back the colour cautiously, drop by drop, with $\frac{n}{5}$ caustic soda. A good lacmoid solution should give a sharper reaction than litmus. For further details regarding such tests, see "Uses" and "Litmus Tincture".

Uses.—The solution of lacmoid has a peculiar reddish colour which instantly turns blue with a trace of alkali. Opinions still differ regarding its value as an indicator, but

Förster holds that when made from good lacmoid it merits precedence over all others, even to litmus tincture, for sharp change of tint and purity of colour. It is said to be particularly well adapted for nitrogen estimations, and to excel litmus for that purpose. On the subject of Förster's investigations, Dr. Niederhäuser, Wiesbaden, informed the present author that he was unable to obtain good results with the indicator. Förster also recommends a lacmoid tincture prepared with the addition of malachite green as being very satisfactory. Niederhäuser has examined many preparations from various sources (purified at once, according to Förster), with and without additions of the various malachite green preparations. Particularly with purified samples, he obtained a very sharp reaction using pure water alone, but in presence of soda and potash salts, and especially ammonia, the end reaction was obscured by a blue-violet fluorescence with a reddish tinge. The solution must be kept in dark bottles, as in course of time it suffers deterioration from access of light, otherwise it is comparatively stable.

Commercial Varieties.—Förster has found lacmoids of very poor quality on the market, and in some instances no blue water-soluble substance was present at all, and the solution in alcohol had a brownish-violet tint which alkalies changed to dark blue.

2. Diazoresorcin (Weselsky's Indicator), ($C_{18}H_{10}N_2O_6$).—Small, dark red crystals, with a greenish metallic lustre, difficultly soluble in alcohol, insoluble in water, and dissolving in alkalies to a blue-violet solution. This so-called diazoresorcin is the colouring matter of lacmoid in a very pure state, and has been proposed as an indicator. The author, from investigation of this substance, considers its action in presence of alkalies places it at a disadvantage, as the solution becomes fluorescent, and this increases with the purity of the preparation. The tests for lacmoid and litmus tincture may be used here.

Crismer recommends the indicator (which is also called resazurin, and which, according to him, possesses the formula $C_{12}H_7NO_4$) for standardising acids by means of borax. He gives a method (loc. cit.) for preparing the same (see also Crismer, "J.S.C.I.," 1896, p. 618).

LACMOID PAPER.—The blue or red paper is prepared by carefully impregnating the paper with purified lacmoid solution; the red paper easily turns blue again, and must be kept in well-stoppered bottles. Förster ("Zeit. f. angew. Chem.," 1890, p. 165) found by comparative tests that ordinary blue litmus paper is only a small degree less sensitive than blue lacmoid, but that red litmus is far excelled by red lacmoid. On the examination of test papers see "Indicators," where the limit of sensitiveness of litmus paper is given; lacmoid ought to be about equal to litmus in this respect. For further details see Förster ("Zeit. f. angew. Chem.," 1894, p. 166).

LACTIC ACID.—Acidum lacticum, pur.: fermentation lactic acid ($C_3H_6O_3$). Mol. wt., 90·06. A clear, colourless, or only very slightly yellow, and odourless liquid of 1·210 sp. gr., containing about 75 per cent. anhydrous lactic acid, and giving clear solutions with water, alcohol, and ether.

Tests for Impurities.—*Appearance, Smell, Solubility.*—As described above.

Oxalic, Citric Acids, etc.—On rendering alkaline with lime water no turbidity must appear either in the cold (oxalic, tartaric, phosphoric acids) or after heating (citric acid). The addition of lead acetate solution, drop by drop, must not produce a precipitate (sulphuric or malic acids).

Lime, Metals, Sulphuric Acid, etc.—When dissolved in 10 parts of water the solution must not be affected by either hydrogen sulphide, barium chloride, silver nitrate, or ammonium oxalate.

Sugar, etc.—On heating slightly, no smell of fatty acids must be detected, nor, on carefully adding sulphuric acid so as to form a layer, must any colour appear.

Quantitative Estimation.—The acid is titrated with normal alkali, 1 c.c. = 0·09 gm. lactic acid. A method depending upon its oxidation to aldehyde is described by Boas ("Deutsche medicin. Wochenschrift," 1893, No. 39). On the testing of lactic acid, see Ulzer and Seidel, "J.C.S.," 1897, A., p. 389.

Uses.—Lactic acid, with the addition of hydrochloric acid, is used as a solvent for albuminoids in milk during the fat estimation with the lactocrite ("J.C.S.," 1892, p. 550). In

1 per cent. solution or stronger, the acid is used for the elimination of lime in microscopy.

Commercial Varieties.—The acid is sold of varying specific gravity and percentage; coloured qualities for technical purposes may also be obtained.

LEAD.—Plumbum (Pb). Mol. wt., 207·2. Soft, bluish-grey metal. M.p., 334°. Lead is easily soluble in dilute nitric acid.

Tests for Impurities.—The analysis of lead is so fully described in well-known works on analytical and technical chemistry that these only require reference here; see Sutton, "Vol. Anal.," 7th ed., p. 222, and Fresenius, "Quant. Anal.," vol. ii., p. 370 *et seq.*

The estimation of silver in lead is a matter of particular importance in certain analytical processes (see "Silver").

The best dry method is cupellation, and the one always adopted. In the factory of Messrs. E. Merck, of Darmstadt, 160 gms. of lead are employed in this test: this quantity is distributed over four cupels and then scorified, and what remains is subsequently cupelled in one dish. The lead tested after this method must be perfectly free from silver, or contain only a maximum amount of 0·001 per cent.; such lead is sufficiently pure to be used as free from silver for assaying purposes.

Quantitative Estimation.—See above.

Uses.—Lead, free from silver, is used analytically for the estimation of silver by the dry method (see above).

Commercial Varieties.—In addition to lead, free from silver, for analysis, ordinary refined lead (soft lead) can be obtained in a very pure state in the market, containing from 99·96 to 99·99 per cent. metal, and also crude lead and hard lead containing 95 to 99 per cent. (Fresenius, "Quant. Anal.," vol. ii., p. 370).

LEAD ACETATE.—Plumbum aceticum puriss. Acetate of lead ($Pb(C_2H_3O_2)_2$, $3H_2O$). Mol. wt., 379·32. Colourless, lustrous, transparent crystals, easily soluble in water, insoluble in alcohol and ether.

Tests for Impurities.—*Alkalies, Alkaline Earths, etc.*—5 gms. of the acetate are dissolved in about 100 c.c. of water and the lead precipitated with hydrogen sulphide. The filtrate is then evaporated to dryness, and on ignition only traces of residue should remain.

Copper and Iron.—2 gms. are dissolved in about 40 c.c. of water, the lead precipitated with ammonia, and the precipitate allowed to settle; the latter must be white, not yellow, and the supernatant liquor must not be coloured blue.

Chlorine.—The solution (1 : 30) must show no change after acidifying with nitric acid and adding silver nitrate solution.

Nitric Acid.—The solution (1 : 30) is rendered faintly blue with a drop of dilute indigo solution; on addition of half the volume of concentrated sulphuric acid the colour must not be discharged.

Quantitative Estimation.—Lead is estimated by precipitation with sulphuric acid as lead sulphate, or as lead sulphide with H_2S. For the analysis of acetate of lead see Sutton, "Vol. Anal.," 7th ed., p. 90, and Fresenius, "Quant. Anal.," vol. ii., p. 378.

Uses and Storage.—In the analysis of inorganic substances lead acetate is used for the estimation of chromic and molybdic acids, and it is further employed for the precipitation of tannins and colouring matter in the analysis of plant juices, and also for the precipitation of such organic acids as malic and oxalic.

Lead paper is prepared by soaking filter paper in pure aqueous solution of acetate of lead, and is used for the detection of hydrogen sulphide.

Acetate of lead should be carefully stored in glass bottles.

Commercial Varieties.—Two varieties of this salt exist in the market under the names of puriss. and commercial. The latter preparation can easily be distinguished by its yellow or blue tinge, and it contains iron, copper, and alkali. The pure commercial acetate often shows a blue colour, which Schneider ("Pharm. Ztg.," 1895, No. 76) concludes is due to a mechanical admixture of prussian blue.

LEAD ACETATE (BASIC).—Basic lead acetate is prepared by boiling 430 gms. of normal lead acetate with 130 gms. of

litharge and 1000 c.c. of distilled water for 1 hour. The solution is then allowed to settle and the clear colourless liquid decanted. This is diluted to 1·25 sp. gr. with recently boiled distilled water. The reagent absorbs carbonic acid from the air yielding a white precipitate of basic carbonate and changing to the normal acetate. It should therefore be kept in small well-stoppered bottles. It is employed for clarifying liquids containing sugar previous to the estimation of the latter by the polarimeter.

See also "Lead Subacetate".

LEAD CARBONATE (BASIC).—Plumbum carbonic. puriss. ($2PbCO_3$, $Pb(OH)_2$). Mol. wt., 775·63. Pure white powder, insoluble in water.

Tests for Impurities.—*Lead, Copper, Alumina, etc.*—These are tested for as recommended under "Lead Oxide," and the tests for nitric acid and chlorine are also detailed there.

Acetic Acid.—On heating in a test tube no darkening should appear.

Quantitative Estimation.—As under "Lead Oxide".

Uses.—Lead carbonate is sometimes used for the precipitation of tannins in vegetable extracts, and on its use as a decolorising and clarifying agent for urine, wines, etc., see Morfarzo, "Pharm. Ztg.," 1898, p. 887.

Commercial Varieties.—Often contain copper and chalk.

LEAD CHROMATE.—Plumbum chromicum pur.: chromate of lead (CrO_4Pb). Mol. wt., 323·2. Heavy powder of a yellowish-brown colour, or in the form of small brown fused lumps. Insoluble in water.

Tests for Impurities.—*Organic Substances.*—No carbon dioxide must be given off on ignition.

Substances Soluble in Water.—5 gms. of the substance are shaken with hot water and filtered; the filtrate must leave no residue on evaporation.

Quantitative Estimation.—According to Mohr ("Titrirmethode," 6th ed., p. 771) the following is a suitable method for the estimation of chromic acid in chromate of lead. The chromate of lead is finely powdered, a quantity is then weighed

out and transferred to a flask together with a weighed quantity of ferrous ammonium sulphate dissolved in a little water, and finally a large number of glass beads are added. The mixture, after having been thoroughly agitated, so as to form a fine emulsion, is treated with dilute hydrochloric acid, and the flask closed with a rubber valve.

The mixture is quickly boiled to drive off air, the flask then placed on a sand bath, and heated till the reaction is over. As decomposition goes on slowly, it is necessary to avoid access of air to prevent oxidation of the ferrous salt. Any undecomposed yellow chromate will be easily detected at the bottom of the flask. Lead chloride separating out also shows a yellow colour in the iron solution, but it can easily be distinguished from the chromate. When all decomposition has ceased the solution is cooled, washed into a beaker and diluted, taking care to wash the glass beads thoroughly, and the remaining ferrous salt titrated with potassium permanganate or bichromate. The estimation is conducted according to the following example: 1 gm. of lead chromate was digested with 4 gms. of ferrous ammonium sulphate: after dilution it required 7·2 c.c. of a standard permanganate solution to produce a permanent red colour. The 4 gms. of ferrous salt contain $\frac{4}{7}$ = 0·591 gm. Fe, and after subtracting 0·072 gm. Fe (= the equivalent of 7·2 c.c. permanganate solution) we obtain 0·519 gm. Fe, which, multiplied by 1·929 gives 1·001, instead of 1 gm. originally taken. The chromate must be previously dried at 100° C. before weighing out.

If the lead is to be estimated, the salt must be decomposed with concentrated hydrochloric acid and alcohol, and a further quantity of alcohol added when cool; the precipitated lead chloride is collected on a filter, dried at 120°, washed with alcohol, and weighed after drying again.

Uses and Storage.—Lead chromate is used in the ultimate analysis of organic compounds to facilitate the combustion of substances troublesome to ignite, and also those containing sulphur. In the combustion of substances which are very difficult to burn it is advisable to add to the chromate 1-10th of its weight of fused and powdered bichromate of potash. Lead chromate must be kept in glass-stoppered bottles, carefully protected against dust.

Note.—We may here mention the ortho plumbates of the alkaline earths, discovered by G. Kassner. Of these the calcium ortho plumbate (Ca_2PbO_4) is said to be particularly suitable for the combustion of organic substances, see also Kwasnik, "Arch. f. Pharm.," vol. ccxxviii., part iv., 1890; and "J.S.C.I.," 1890, p. 187; 1891, p. 160.

Commercial Varieties.—Chromate of lead can be obtained in the market for technical and analytical purposes. For technical purposes the neutral chromate of lead (chrome yellow) is employed as a colour, as also the basic chromate of lead (chrome red) and a mixture of basic and neutral chromate under the name of chrome orange. The colour of the basic salt varies, according to its method of preparation, from a dark vermilion to a dull red lead colour. In the neutral salt it varies from lemon-yellow to reddish-yellow, and, after fusion, to a dark brown. The commercial chrome colours are sometimes adulterated with clay, barytes, lead sulphate,[1] plaster of Paris, and chalk. For analytical purposes lead chromate, pure fused and pure powdered, are obtainable in the market.

The former is prepared by melting the pure neutral salt. As the neutral salt, on being heated above the melting point, decomposes into chromic oxide and basic salt, the fused chromate of lead nearly always contains the basic salt. On the subject of impurities in chromate of lead, used for ultimate organic analysis, H. Ritthausen and N. N. Lubavin draw attention to the presence of carbon dioxide[2] ("Zeit. f. anal. Chem.," 1887, p. 629). Nencki asserts that he has detected in a lead chromate obtained from a chemical factory in Northern Germany, a deliberate adulteration with lead oxide ("Anzeiger der Akademie der Wissenschaften in Wien," 1889, No. 11, and "J.S.C.I.," 1889, p. 822). On this point the present author would like to remark that the method Nencki employed to detect the adulteration is wrong. Nencki treated the chromate

[1] Chrome yellows usually contain more or less sulphate of lead which cannot be regarded as an adulterant.

[2] Recent researches have shown that it is not possible to supply a lead chromate absolutely free from CO_2. On heating in a combustion tube and testing the gas with barium hydrate there is always an unavoidable turbidity. It is therefore necessary to ignite the lead chromate immediately before the combustion test, as in the case of copper oxide.

with dilute acetic acid, and from the fact of some lead dissolving in the acetic acid he came to the conclusion that it had been adulterated with oxide, but as it is well known that basic chromate of lead dissolves in acetic acid, and as the basic salt is readily formed in fused chromate of lead (*q.v.*), it must not be concluded that the lead chromate had been adulterated with oxide because some lead was dissolved by acetic acid. The best and safest method of detecting adulteration is to quantitatively estimate the lead and chromic acid as recommended above by the author. For other impurities, such as plaster of Paris, barytes, etc., which, as already remarked, are found as admixtures in commercial chrome colours, see C. O. Weber, "J.S.C.I.," 1885, p. 671.

The author has examined the pure lead chromate from various factories without finding adulteration, but a few of the samples were not carefully prepared, and evolved carbon dioxide on ignition.

LEAD OXIDE.—Plumb. oxydat. puriss.: oxide of lead (PbO). Mol. wt., 223·2. Pure lead oxide is a lemon coloured or reddish-yellow powder. Insoluble in water.

Tests for Impurities.—*Metallic Lead, Copper, Alumina, Carbonic Acid, etc.*—5 c.c. of water are poured over 2 gms. of the lead oxide in a test tube, and then acetic acid slowly added in excess. No evolution of carbonic acid should take place. The solution obtained in this way should be clear or only slightly cloudy, and should leave only a very small amount of residue. The acetic acid solution is precipitated with sulphuric acid; the filtrate should neither show a flocculent precipitate of alumina nor a blue colour on addition of ammonia in excess. On adding oxalate of ammonia to this solution no turbidity, or only a very slight one, should appear.

Nitric Acid and Chlorine.—On colouring a dilute acetic acid solution of lead oxide with a drop of indigo solution, and adding concentrated sulphuric acid, the blue colour should not disappear. A solution (1 : 30) in dilute nitric acid must not show a cloudiness on addition of nitrate of silver solution.

Quantitative Estimation.—The lead oxide is dissolved in dilute acetic acid and the lead precipitated with hydrogen

sulphide. The precipitate of lead sulphide is washed, dried, and ignited in a current of hydrogen, and after adding some flowers of sulphur and again igniting, weighed. For details as to this method and others for the estimation of lead, see, *inter alia*, Fresenius, "Quant. Anal.," vol. i., p. 241; vol. ii., p. 376. Fresenius (loc. cit.) describes a method for examining commercial lead oxides.

Uses and Storage.—Pure lead oxide is used in the analysis of organic substances containing chlorine, bromine, or iodine (Fresenius, "Quant. Anal.," vol. ii., p. 68). It is used further for the saponification of fats and for effecting the solution of minerals by fusion, and should be stored with the same precautions as the chromate.

Commercial Varieties.—The author has examined samples of plumb. oxydat. puriss. from various sources, and has several times found them to contain a considerable quantity of lead carbonate (10-20 per cent.). They often contain also alumina and copper, and some samples have a red colour owing to the presence of a considerable quantity of red lead.

In addition to pure lead oxide, "litharge," used for technical and pharmaceutical purposes, can be obtained in the market The impurities of this preparation are chiefly metallic lead, red lead, copper, lead carbonate, and calcium carbonate. Salzer ("Rep. d. Chem.-Ztg.," 1889, p. 26) found basic lead nitrite in a sample; this litharge was evidently obtained as a by-product in the manufacture of nitrites. E. Reichardt ("Rep. d. Chem.-Ztg.," 1889, p. 257) detected in commercial litharge 14·55 per cent. barytes. Methods for the examination of "litharge" and "red lead" (Pb_3O_4), a product sold for technical purposes, are described in textbooks on analytical chemistry. On the purity of commercial red lead the following observations by R. Frühling ("J.S.C.I.," 1889, p. 203) may be cited:—

"Red lead employed for trade purposes (colours, lacquers, cements) may leave an insoluble residue of about 10 per cent. on treatment with nitric acid and sugar. The better class of red leads for pharmaceutical use must only leave about 1 per cent. residue. On analysis of nine samples, one left a residue of 2·08 per cent., five between 8 and 10 per cent., another 17·66 per cent., and two between 25 and 27 per cent. The residue

consisted in six instances of clay and fine sand, in three cases of finely ground barytes, doubtless an adulteration, and one sample obtained from a druggist's shop gave 1·25 per cent. residue."

LEAD PEROXIDE.—Plumbum peroxydatum puriss. (PbO_2). Mol. wt., 239·2. Heavy, dark brown powder, insoluble in water.

Tests for Impurities.—*Lead Nitrate, Chlorides, Lime, Soda, etc.*—5 gms. of peroxide are boiled with about 60 c.c. of water, along with a little dilute nitric acid, and then filtered; one part of the filtrate must give no precipitate with silver nitrate solution, another must only leave traces of residue on evaporation (lime or lead).

Sulphuric Acid.—5 gms. of the peroxide are digested for several hours with a concentrated solution of pure sodium bicarbonate, filtered, and the filtrate, after adding excess of hydrochloric acid, tested for sulphuric acid with barium chloride.

Manganese.—Some of the peroxide is heated with concentrated sulphuric acid till perfectly decomposed, and the cooled mixture treated with water and a fresh quantity of peroxide; on renewed heating a red solution of permanganic acid is obtained if manganese is present.

Note.—L. de Koninck ("J.S.C.I.," 1889, p. 215) calls attention to the fact that it is not sufficient to boil a sample with dilute nitric acid for the detection of manganese present as peroxide in the lead, but that the above test must be used. It is quite a matter of general occurrence to find the commercial varieties giving this manganese reaction.

Quantitative Estimation.—According to Ebell ("J.C.S.," 1886, A., p. 742) the iodine method is the best, and is carried out as follows:—

0·5 gm. of the peroxide is covered with water in a small flask, well mixed by shaking, and then a large excess of concentrated hydrochloric acid added. The flask is provided with a Varrentrap bulb apparatus, filled with potassium iodide, and the end inserted into the flask by means of a rubber cork; the flask is then gently heated. The lead peroxide is dissolved to the tetrachloride ($PbCl_4$), and only traces of chlorine escape into the potassium iodide solution. The potassium iodide

solution from the receiver is now run into the cooled flask, and, after transferring to a beaker and diluting to about 300 c.c., the iodine liberated is titrated with thiosulphate solution.

On other methods for estimation of PbO_2, see Ebell, "Rep. anal. Chem.," vol. vi., pp. 141-143.

Uses and Storage.—Lead peroxide is used in qualitative analysis for the detection of manganese. In ultimate organic analysis it is used for the combustion of substances containing sulphur (the sulphur of the compound is obtained after combustion with peroxide in the form of lead sulphate).

According to Vortmann ("J.C.S.," 1886, A., p. 648; 1885, A., p. 836), lead peroxide can be used for the direct estimation of chlorine in presence of bromine. On the colour reaction which certain alkaloids give with lead peroxide, see Ihl ("Chem.-Ztg.," 1889, p. 95). The use of peroxide has also been suggested for the separation of nickel and cobalt ("Zeit. f. anal. Chem.," 1891, p. 230). It must be stored in the same way as lead chromate.

Commercial Varieties.—Besides pure lead peroxide, the raw product used in the manufacture of matches, etc., can be obtained. The latter often contains considerable quantities of lead nitrate, and is generally employed in a moist condition, as it is obtained by decomposing red lead with nitric acid.

LEAD SUBACETATE.—Liquor plumbi subacetici. Clear, colourless, alkaline liquid. Sp. gr., 1·235 to 1·240.

Tests for Impurities and Quantitative Estimation.—As in "Lead Acetate".

Uses and Storage.—Subacetate of lead is prepared by digesting a solution of acetate of lead with lead oxide, as prescribed by the German Pharmacopœia (iii.). It is used for identifying benzoic and formic acids, etc., and is especially employed in the analysis of vegetable matter as a precipitant and clarifier. It must be stored in small bottles, and protected from the atmosphere as it absorbs carbonic acid and yields a deposit of carbonate.

LITMUS.—Large blue grains partly soluble in water, deep blue solution.

Tests.—The quality of the samples may be gauged by

comparison of shade and depth of colour in the cold, aqueous extract. For this purpose equal quantities of the samples to be compared are weighed out, the same amount of cold water added to each, and the solutions allowed to stand, with occasional shaking, at the room temperature for 12 hours; after standing overnight to settle, a portion is filtered off and tested colorimetrically, as under "Carmine," p. 73. It is better to prepare a tincture of litmus, which may be made from the aqueous extract obtained as above by gently boiling and adding hydrochloric acid drop by drop, until a permanent wine-red colour is obtained after boiling for 7 or 8 minutes. The solution is then allowed to cool, and an equal volume of strong alcohol added. The tincture is then tested for degree of sensitiveness towards acids and alkalies (see "Litmus Tincture,") and also colorimetrically as above. The best method of preparing litmus solution, however, is to extract with boiling water, filter, add acetic acid in slight excess to the filtrate, evaporate to dryness, wash the residue several times with alcohol, then dry, and dissolve in water to form a strong solution, neutralise with dilute NaHO, and preserve with a few drops of carbolic.

Uses.—For the preparation of the tincture. The colouring matter in litmus consists of erythrolitmin and azolitmin, with ammonia, potash, and lime, according to Kane (see "Azolitmin").

Commercial Varieties.—These vary considerably with regard to quality, usually containing large quantities of carbonate of lime, and some specimens are almost too inferior to be used for analytical purposes. A purified form is sold under the name "Lackmus Puriss".

LITMUS TINCTURE.—A wine-red solution, of alcoholic odour.

Tests.—One litre of distilled water in a Jena glass[1] flask is kept boiling gently for 8 or 10 minutes, and then quickly cooled. The water ought now to be free from CO_2; two or three quantities of 250 c.c. each are then transferred to flasks

[1] Reinitzer ("J.C.S.," 1895, A., ii., p. 134) has investigated the effect produced on the titration when the boiling is conducted in vessels made of ordinary glass containing alkali.

which have been previously rinsed out with a little of the water; a few drops of litmus tincture are then added until a distinct violet colour is produced. With well-prepared tinctures the colour ought to be very decided, and ought to be free from a blue or red tinge. On adding a drop of $\frac{n}{10}$ hydrochloric acid to one of the solutions a wine-red colour should at once appear, and, on adding the same amount of $\frac{n}{10}$ alkali to another a pure blue colour ought to be produced. Both tests will show a slight violet tinge on standing even for a minute, and each will use 2 drops of acid and alkali respectively to restore them to the tint formerly obtained with 1 drop.

Note.—Reinitzer ("Zeit. f. angew. Chem.," 1894, p. 550) employs the above test in comparing various indicators. Particular attention is there called to the fact that this extreme sensitiveness only exists where a cold solution is concerned; the above remark regarding the return of the violet colour on standing is also enunciated. On the testing of the tincture for sensitiveness, see Lunge, "Zeit. f. angew. Chem.," 1894, p. 733 *et seq*, and "J.C.S.," 1895, A., ii., p. 242. Litmus cannot be used in gaslight as the end reaction is then difficult to observe.

Uses and Storage.—This form of litmus solution is the one most generally used, and forms evidently one of the most delicate indicators. The absence of carbonic acid is essential, and even the small quantity always present in normal potash solutions may give rise to inaccuracies. Liquids to be titrated must be boiled from 7 to 10 minutes and cooled before use. Reinitzer mentions what precautions ought to be taken when titrating. The tincture should be kept in a wide-mouthed bottle, and the quantity required for immediate use drawn up by a glass tube, slightly conical at one end. It is advisable that the tube should contain a little glass wool. If the bottle is tightly corked the colour is discharged, owing, it is said, to the reducing influence of a micro-organism, but the leuco compound formed easily turns blue again in contact with air. Numerous methods for the preparation of a good litmus tincture are recorded in Böckmann's "Chem.-techn. Untersuch," 3rd ed., vol. i., p. 112 *et seq*. See also above.

LITMUS PAPER, BLUE, RED, AND NEUTRAL.—The paper must be uniformly, but not too strongly, coloured.

According to Dieterich's table, the sensitiveness of blue litmus paper towards hydrochloric acid reaches its limit in a solution containing 1 part of the acid to 50,000 parts of water, and the red paper in 1 part of caustic potash to 20,000 of water. The delicacy of the test papers may be determined on solutions so prepared, but such dilute solutions keep very indifferently, and ought frequently to be freshly prepared. On the preparation, etc., of sensitive test papers, see pp. 143, 339. On the sensitiveness of litmus paper, see Ronde, "Pharm. Ztg.," 1896, p. 736. Neutral litmus paper, prepared with note-paper, is specially recommended by Böckmann, as presenting an extremely sensitive test paper, equally serviceable for the detection of acids or bases. The papers should be kept in bottles and carefully protected from ammonia or acid fumes, as their delicacy is easily destroyed.

LOGWOOD TINCTURE.—*Preparation.*—Tincture of logwood is prepared by extracting logwood chips with weak alcohol or by dissolving logwood extract in a mixture of alcohol and water.

It is a deep-red liquid becoming purple-red on addition of ammonia.

It is employed for the detection of alum in flour and bread, for which purpose it is evaporated on the material. If alum is present the residue has a fine blue colour, but if this substance is absent the residue is a dull red. Similar colours are given with copper and other metals. It is also employed for detecting mineral acids in vinegar (Ashby, Allen's "Organic Analysis," vol. i.).

See also "Haematoxylin".

LUTEOL, $C_6H_2OH_2(NC) . (C_6H_5)_2Cl$.—Yellowish needles, m.p., 246°. Soluble in alcohol and in ether. Used as an indicator giving with alkalies an intense yellow colour.

MAGNESIUM.—Magnesium metallicum. At. wt., 24·32. Metal of brilliant lustre, almost resembling silver, soluble in dilute acids.

Tests for Impurities.—Magnesium has been recommended by various authors as a substitute for zinc in testing for

arsenic, but it is worthy of note that Flückiger was unable to obtain magnesium which did not contain very slight traces of arsenic and sulphur ("Arch. d. Pharm.," 1889, p. 11; and "J.C.S.," 1889, A., p. 650). The metal has also been proposed for the reduction of ferric to ferrous compounds in the volumetric estimation of iron, for which purpose it must be free from the latter; that is to say, a solution of the metal in about 1 c.c. of sulphuric acid ought not to decolorise dilute permanganate solution (see "Zinc"). The author has examined various samples of magnesium, but in no instance did they stand Marsh's test or the test for iron. The metal reacts strongly with oxides and chlorides at a high temperature, and even in neutral aqueous solution most metallic chlorides give up their chlorine (see Seubert and Schmidt, "Annal. d. Chem.," 1891, vol. cclxvii., p. 218 *et seq.*). On the preparation and use of "magnesium amalgam," see Fleck and Bassett, "Journ. Amer. Chem. Soc.," 1895, 17, p. 789.

Commercial Varieties.—It is sold in the form of wire, powder, ribbon, and bar.

MAGNESIUM CARBONATE.—Magnesium carbonic.: carbonate of magnesia ($MgCO_3$). Mol. wt., 84·32.[1] White, flocculent mass, or light powder, insoluble in water.

Tests for Impurities.—*Iron Alkalies, etc.*—The solution in dilute hydrochloric acid should be colourless; on boiling the salt with water and evaporating the filtrate only a slight residue should remain.

Note.—The presence of iron and manganese colours the hydrochloric acid solution; sand, silicic acid and silicates remain undissolved. On mixing 5 gms. with 40 c.c. of water and heating to boiling at once, 20 c.c. of the filtrate should not leave more than 0·015 gm. residue on evaporation; a larger residue indicates the presence of alkaline salts.

Metals, Alumina, Lime, Sulphuric Acid, and Chloride.—The solution in dilute acetic acid (1 : 50) must be clear and give no reaction with hydrogen sulphide. On boiling the

[1] The composition of magnesium carbonate varies according to the salt of magnesia from which it is prepared, the precipitating agent, and the temperature observed during both precipitation and drying. It is usually more or less basic.

original solution, adding ammonia and ammonium oxalate, only a slight turbidity should appear within a few minutes. The addition of barium nitrate solution, and, after acidifying with nitric acid, silver nitrate solution must cause only a slight turbidity.

Uses.—Magnesium carbonate is used as a base for the preparation of other magnesium salts.

Commercial Varieties.—A heavy magnesium carbonate about three times as heavy as the light form, and prepared by precipitating magnesium sulphate solution in the cold, is sold in this country. The light carbonate is used in medicine. Hager states that, on an average, the commercial carbonate consists of 40 per cent. magnesia, 35 per cent. carbon dioxide, and 25 per cent. water; such samples have also been found to contain from 1·25 to 2·15 per cent. of lime, and about 0·25 per cent. oxide of iron.

MAGNESIUM CHLORIDE.—Magnesium chloratum, puriss.: chloride of magnesium ($MgCl_2$, $6H_2O$). Mol. wt., 203·34. White, hygroscopic crystalline mass (prisms).

Tests for Impurities.—*Solubility.*—2 gms. dissolved in 10 c.c. of alcohol must give a clear solution.

Sulphuric Acid.—The solution (1 : 20) must give no reaction with barium chloride.

Phosphoric Acid and Arsenic Acid.—3 gms. are dissolved in 20 c.c. of water, ammonium chloride and ammonia added in excess, and the solution allowed to stand for some time; no precipitate or turbidity must appear.

Metals, Lime, etc.—The solution (1 : 20) must give no reaction with hydrogen sulphide. On adding a sufficiency of ammonium chloride to the aqueous solution (1 : 20), and subsequently ammonia, ammonium oxalate and ammonium sulphide, no turbidity should appear.

Ammonia.—No ammonia should be given off on heating with caustic soda.

Quantitative Estimation.—The magnesia is estimated as pyrophosphate; excess of ammonia and ammonium chloride are added to a solution of the salt; the clear liquid is then mixed with a solution of sodium phosphate and allowed to stand for some time. The precipitate is then collected on

a filter, washed with water containing some ammonia, ignited and weighed as magnesium pyrophosphate. Lime when present must be previously removed by precipitation with ammonium chloride and ammonium oxalate. The chloride in the salt may be estimated by acidifying the solution with nitric acid, and precipitating with silver nitrate.

Uses and Storage.—The salt is used for the preparation of magnesia mixture, as is also the sulphate. It is likewise used for testing ammonium sulphide; it must be well protected from air.

Commercial Varieties.—Ordinary pure magnesium chloride and also a form used for technical purposes are on the market. The latter variety is obtained in large quantities as a by-product from the Stassfurt salt industry, and generally contains a quantity of sulphates and soda, evidenced by its imperfect solution in alcohol. The former variety nearly always contains traces of the sodium salt, and bromides may also be present.

MAGNESIA MIXTURE.—*For Phosphoric Acid Estimation.*—The following method for the preparation of magnesia mixture appears in the "Chem.-Ztg.," 1895, p. 1420: 100 gms. of pure crystallised magnesium chloride and 140 gms. ammonium chloride are dissolved in 700 c.c. ammonia solution (8 per cent.) and 1300 c.c. of water. After standing for several days the solution is filtered. Some chemists prefer to prepare the mixture as follows: 550 gms. magnesium chloride and 1·050 gms. ammonium chloride are dissolved in water, then $3\frac{1}{2}$ litres concentrated ammonia solution (sp. gr. 0·91) are added and the solution diluted to 10 litres. The action of magnesia mixture on the vessels containing it is described in a paper by L. de Koninck ("Chem.-Ztg.," 1895, p. 450, and "J.S.C.I.," 1895, p. 691). This author ascribes the formation of scales resembling mother of pearl, which form on long standing in glass vessels, to a decomposing action of the mixture on glass. A most interesting point in de Koninck's experiments is that a glass vessel which had been steamed[1] for some time was

[1] In Professor Ostwald's laboratory all flasks and bottles used for delicate work are steamed for some time, thus rendering them more resistant to the action of chemical reagents.

scarcely attacked at all after fifteen months, whereas a bottle merely rinsed out with water was so strongly attacked on standing for the same time that the surface was completely coated with a film of magnesium silicate (" Chem.-Ztg.," 1896, p. 129).

MAGNESIUM OXIDE. — Magnesium oxydatum purum: calcined magnesia (MgO). Mol. wt., 40·32. Fine, very light, white powder. Only very slightly soluble in water (1 : 55,000).

Tests for Impurities.—*Carbonic Acid.*—A small quantity of the oxide is heated with a few c.c. of water, and the mixture poured into a few c.c. of dilute acetic acid; solution must take place without effervescence, only a few solitary bubbles of gas appearing.

Metals, etc.—As under " Magnesium Carbonate," p. 180.

Quantitative Estimation.—The sample is first dissolved in hydrochloric acid, and then treated as under " Magnesium Chloride ".

Uses and Storage.—The salt is used in the analysis of iron (see also the following article on " Magnesium Oxide, free from Sulphuric Acid "), and for the estimation of ammonia. It must be carefully protected from the atmosphere. In testing for ammonia the magnesia should be almost free from carbonic acid, otherwise the operator may be misled.

Commercial Varieties.—These sometimes contain considerable quantities of carbonic anhydride, sulphuric acid and lime. The magnesia described in the following article is used for special analytical work.

Magnesium Oxide (MgO). **Free from Sulphuric Acid.**—A white powder, evolving only slight traces of CO_2 with dilute acids.

Sulphuric Acid.—3 gms. are dissolved in a little hydrochloric acid, the solution diluted to about 100 c.c. heated to boiling, and barium chloride added; after 12 hours' standing no precipitate should appear.

Note.—As the commercial oxide and carbonate always contain traces of sulphuric acid, this variety has therefore to be specially prepared for estimations where the absence of sulphuric acid is essential (iron estimations).

MAGNESIUM SULPHATE.—Magnesium sulphuric. puriss.: sulphate of magnesia ($MgSO_4$, $7H_2O$). Mol. wt., 246·49. Small, colourless rhombic crystals, soluble in water (1 : 2) giving a neutral reaction in aqueous solution.

Tests for Impurities.—*Solubility.*—The aqueous solution (1 : 10) must be clear and have no effect on litmus paper.

Phosphoric and Arsenic Acids, Metals, etc.—As under "Magnesium Chloride," p. 181.

Note.—Marsh's test may also be applied. The third German Pharmacopœia prescribes the following test for arsenic: On shaking together 1 gm. of the finely-powdered sample and 3 c.c. of stannous chloride solution, no colour must appear within an hour.

Chlorine.—The aqueous solution (1 : 20) must give no reaction with silver nitrate.

Sodium Salt.—When ignited on platinum wire no permanent yellow flame must be apparent.

Quantitative Estimation. — See under "Magnesium Chloride". The sulphuric acid may be determined as barium sulphate.

Uses.—See "Magnesium Chloride".

Commercial Varieties.—These often contain a large quantity of chloride, and the presence of arsenic has frequently been detected. The crude salt has generally a grey appearance, and contains various impurities which may be detected by the foregoing tests. Magnesium sulphate may readily be distinguished from Glauber's salts by adding sodium phosphate, which gives a crystalline precipitate with the aqueous solution of the magnesium salt, in presence of ammonia and ammonium chloride. As zinc sulphate strongly resembles the magnesium salt in appearance, any mistake may be avoided by adding ammonium sulphide.

MANGANOUS CHLORIDE. — Manganum chlorat. cryst. pur. ($MnCl_2$, $4H_2O$). Mol. wt., 197·91. Pink monoclinic crystals, easily soluble in water (2 : 1) to a clear solution.

Tests for Impurities. — *Sulphuric Acid.* — The clear, aqueous solution (1 : 10) must give no reaction with barium chloride.

Iron, Other Metals, etc.—As under "Manganous Sulphate," p. 187.

Chlorine.—A solution (1 : 20) to which dilute sulphuric acid has been added must not turn blue on the addition of starch solution containing zinc iodide.

Quantitative Estimation and Uses. — See "Manganous Sulphate".

Manganous chloride solution is also used for the determination of oxygen by Winkler's process (see L. W. Winkler, "J.S.C.I.," 1889, p. 727).

Commercial Varieties. — Crude manganous chloride and also sulphate are placed on the market, the former being obtained in large quantities as a by-product in the manufacture of chlorine. The salt generally contains a considerable amount of sulphuric acid, lime, iron, and also arsenic. A pure fused chloride is also sold.

MANGANESE DIOXIDE.—Manganum peroxidatum : pyrolusite (MnO_2). Mol. wt., 86·93. Steel-grey lumps, with a metallic lustre. Good pyrolusite, when powdered, should have the above appearance, and contain about 90 per cent. MnO_2.

Tests for Impurities.—For the valuation of pyrolusite a quantitative analysis is made.

Quantitative Estimation.—The mineral is used on the large scale in the manufacture of chlorine and bleaching powder,[1] and in analytical work for the preparation of chlorine and oxygen; the value of the substance chiefly depends upon the amount of dioxide present. Various reliable methods have been proposed for its estimation by such chemists as Bunsen, Fresenius, Will, and Lunge, that by the latter being especially good. Lunge's method is accepted officially by the German soda manufacturers, and is conducted as follows: 1·089 gms. of the finely powdered sample, which has been dried for some time at 100°, are weighed out and transferred to a strong flask provided with a Bunsen india-rubber valve; to this are added 75 c.c. (three quantities from a 25 c.c. pipette) of a solution of

[1] $MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$. Theoretically, 87 parts by weight of manganese dioxide and 142 parts by weight of hydrochloric acid (absolute) evolve 71 parts by weight of chlorine. From 100 kilograms of good pyrolusite (about 90 per cent.) and about 500 kilograms of ordinary hydrochloric acid a yield of practically 70 kilograms chlorine is obtained.

100 gms. pure iron sulphate, and 100 c.c. pure concentrated sulphuric acid in a litre of water; this solution must, however, be previously standardised on seminormal permanganate (15·800 gms. chemically pure salt per litre), the strength of which has been checked on the day it is used. The same 25 c.c. pipette must also be employed. The acid iron solution must be diluted with from four to eight times its volume of distilled water. The flask is then closed with a cork, into which a valve is fitted, and the solution heated until the MnO_2 has been decomposed (which may be noted by the residue ceasing to show a dark colour). During cooling the valve must fit tightly, which may be seen from the rubber contracting. When quite cold, 200 c.c. of water are added, and the solution titrated with permanganate until, on shaking, the pure colour remains for at least 30 seconds; disappearance of colour after this is unimportant. The quantity of permanganate used is subtracted from the amount equivalent to the 75 c.c. of iron solution, each c.c. of the remainder being equivalent to 0·02178 gm. (or 2 per cent.) MnO_2.

It is often the custom of manufacturers to estimate the moisture and carbon dioxide which may be present in pyrolusite, as well as the amount of hydrochloric acid employed in its decomposition. Further details regarding the analysis of pyrolusite may be obtained in Böckmann, "Chem.-techn., Untersuch.," 3rd ed., vol. i., p. 440 *et seq.*

Uses.—See under "Quantitative Estimation".

Commercial Varieties.—These vary greatly in percentage and appearance, some samples containing as little as 30 per cent. MnO_2. Good pyrolusite may be recognised by its steel-grey colour, especially when powdered, poorer qualities presenting a brown or reddish-brown appearance.

MANGANESE METAPHOSPHATE.—See "Metaphosphoric Acid," p. 226.

MANGANESE SULPHATE. — Manganum sulphuricum puriss. cryst. ($MnSO_4$, $4H_2O$). Mol. wt., 223·05. Rose-coloured rhombic crystals, easily soluble in water (2 : 1·6). The aqueous solution (1 : 20) should be clear and neutral, or only slightly acid.

Tests for Impurities.—*Solubility.*—See above.

Iron, Other Metals, etc.—On heating the aqueous solution (1 : 20) with a few drops of hydrochloric acid and chlorine water, and adding potassium sulphocyanide, no red colour must appear; the solution must give no reaction with excess of hydrogen sulphide. On precipitating the manganese from a solution of 3 gms. of the salt by means of ammonium carbonate, a filtrate must be obtained which leaves no weighable residue on evaporating and igniting. On dissolving a mixture of the salt and sodium acetate in ten times the quantity of water, and adding a few drops of acetic acid, the addition of hydrogen sulphide must produce no turbidity (Pharm. Germ. iii.).

Chlorine.—The solution must give no reaction with silver nitrate.

Quantitative Estimation. — By the following method—precipitation as sulphide—the manganese may also be separated from alkaline earths, if present. The dilute solution of the salt, to which ammonium chloride is added, is neutralised with ammonia and boiled; ammonium sulphide is then added in excess, and the mixture allowed to stand for some time. The precipitate is then quickly filtered and washed with water containing ammonium sulphide. The dried sulphide is now mixed with sulphur, ignited in a current of hydrogen, and weighed as manganous sulphide. The ammonium sulphide used must be free from carbonate. The detection of other metals, and their separation from manganese may be effected by means of the tests given above.

Uses.—Pure manganese sulphate, free from iron, is used in the estimation of oxygen in water ("J.S.C.I.," 1889, p. 923); also, according to E. F. Smith, for the quantitative estimation of boric acid.

Commercial Varieties.—A pure, partially dehydrated form ($MnSO_4$, H_2O) is sold, as well as the crude salt, which sometimes contains large quantities of chlorides, iron, and other impurities. The water of crystallisation in manganous sulphate varies with the temperature at which crystallisation takes place; between 20° and 30° the salt contains four molecules of water.

MERCURY.—Hydrargyrum metallicum depurat. (Hg). At. wt., 200·6. A liquid metal, volatilising on heating without leaving a residue, and always showing a bright surface.

Tests for Impurities and Quantitative Estimation.—Mercury, which still retains its bright appearance after having been thoroughly agitated with air and which volatilises perfectly, is sufficiently pure for most analytical purposes. Regarding its analysis, see Fresenius, "Quant. Anal.," vol. i., p. 248. The absence of more than mere traces of other metals may be shown by the following test of the American Pharmacopœia: A mixture consisting of 5 gms. of the metal, 5 c.c. of water, and 4·5 gms. sodium thiosulphate are boiled together in a test tube for about 1 minute; the metal must not lose its metallic lustre, and must show only a faint yellow tint.

Note.—According to Graham-Otto, the commercial metal, although sometimes fairly so, is never absolutely pure, as other metals are always present in greater or lesser degree, particularly lead, tin, bismuth, and copper; there is also generally an admixture of dust and other impurities. A greyish skin may sometimes be observed on the surface of the metal, the drops becoming less rotund in proportion to the quantity of these impurities present; the mobility is also affected in like manner. Impure mercury, on being shaken up with air, leaves a skin adhering to the sides of the vessel. Ulex states that one four-thousandth part of lead may be detected in this way.

Uses.—The metal is used in eudiometers, nitrometers, and various apparatus employed for gas analysis, also for the estimation of nitrogen by Kjeldahl's method. The pure redistilled mercury, obtained by treating the metal with nitric acid and distilling, is used for some purposes.

Commercial Varieties.—See note above.

MERCURIC CHLORIDE—MERCURY BICHLORIDE.—Hydrargyrum bichloratum ($HgCl_2$). Mol. wt., 271·52. White rhombic crystals, soluble in water (1 : 14) alcohol, and pure ether. The aqueous solution must give a black precipitate with hydrogen sulphide.

Tests for Impurities.—*General Impurities.*—The filtrate from the hydrogen sulphide precipitate must leave no weighable residue on evaporation.

Arsenic.—On digesting the precipitate from the above with

dilute ammonia and acidifying with hydrochloric acid no yellow precipitate or colour must appear.

Mercurous Chloride.—2 gms. of the finely ground sample must dissolve completely in about 15 c.c. of pure ether.

Quantitative Estimation.—The metal may be estimated volumetrically by Mohr's method (see Sutton's "Vol. Anal.," p. 238). This method is based on the fact that mercuric chloride in alkaline solution is reduced to mercurous chloride by a ferrous salt, with conversion of the latter into the ferric state. The excess of ferrous salt is then titrated with permanganate, the latter being previously standardised on pure iron double salt. Fe × 4·8625 = $HgCl_2$. The mercury may also be precipitated with hydrogen sulphide, and weighed as sulphide; if, however, the samples stand the above tests a quantitative estimation will be superfluous for most purposes.

Schuyten ("J.C.S.," 1897, p. 161) recommends a process for the estimation of mercury salts, combining speed with accuracy and depending on the reaction with sodium peroxide.

Uses and Storage.—It is used for the detection of hydriodic acid, formic acid and tin; also as a test for alkaloids and for the preparation of Bohlig's and Nessler's reagent. It is a violent poison, therefore great precautions must be used in storage.

Commercial Varieties.—Lenz ("Zeit. f. anal. Chem.," 1883, p. 391) comments on the fact that the commercial salt often leaves a considerable residue on solution.

Nessler's Reagent.—The solution may be prepared by stirring together a mixture of 35 gms. potassium iodide and 13 gms. mercury bichloride in 800 c.c. of water and boiling until a clear solution has been obtained. A cold saturated solution of mercury bichloride is now added drop by drop till the precipitate just ceases to redissolve; 160 gms. caustic potash or 120 gms. caustic soda are now added along with a little of the bichloride solution and the liquid allowed to settle. The clear solution has a slightly yellow tint, and on adding 2 c.c. to 50 c.c. of water containing 0·05 mgm. of ammonia must immediately show a yellowish-brown coloration. The reagent should be kept in small, well-stoppered bottles.

MERCURIC NITRATE.—Hydrargyrum nitricum oxydatum. $2Hg(NO_3)_2 + H_2O$. Mol. wt., 667·26. White crystals soluble in water.

Tests for Impurities.—The solid should leave no residue on gentle ignition. It should dissolve to a clear liquid in water, and should give no reaction for sulphates or chlorides.

Uses.—Mercuric nitrate in solution with nitric acid is employed for precipitating the casein from milk previous to estimating the sugar by the polariscope, also in the testing of milk for gelatin.

Millon's Reagent.—This is prepared by dissolving mercury in its own weight of nitric acid, diluting with an equal volume of water and decanting the clear liquid. It is employed for the detection of albuminous substances with which it gives a brick-red colour on heating.

Acid Mercuric Nitrate.—A solution produced by dissolving mercury in twice its weight of nitric acid and diluting the solution with 25 times its weight of water is used for detecting and estimating vanillin with which it gives a violet coloration (C. Estes, "J. Ind. Eng. Chem.," 1917, pp. 142-144).

MERCURIC NITRATE SOLUTION.—This solution is used for the quantitative estimation of urea, and may be formed by dissolving 77·2 gms. of pure red mercuric oxide, previously dried at gentle heat on the water bath, in nitric acid. The solution is evaporated until it has a syrupy consistency, and is then diluted to a litre with water. Any basic salt which may have formed on dilution is redissolved by a few drops of dilute nitric acid. 10 c.c. of this solution are equivalent to 0·1 gm. urea.

MERCURIC NITROSO-NITRATE SOLUTION. — Millon's Reagent, and other Solutions of Mercuric Salts.—*Millon's Reagent* for albuminoids, etc., may be prepared as follows: 10 gms. of mercury are placed in a small flask, and 25 gms. of nitric acid, sp. gr. 1·185, with 25 c.c. of water, are added; the mixture is then kept in a lukewarm place and occasionally shaken till the mercury has dissolved. This is then mixed with a solution of 10 gms. of mercury in 22 gms. nitric acid of 1·250 to 1·300 sp. gr., dissolved at the ordinary temperature.

A simpler method is recommended by Nickel ("Chem. News," vol. lx., 1889, p. 104), and is as follows: 1 gm. of mercury is dissolved in 9 c.c. of fuming nitric acid, sp. gr. 1·52, and the solution diluted with an equal volume of water. On long keeping, this solution becomes inactive, but the addition of potassium nitrite will restore its properties. For details see Nickel (loc. cit.).

Hoffmann's Reagent and Pfugge's Reagent are described in "Chem. News," vol. lx., 1889, p. 104.

Sachsse's Standard Mercuric Iodide and Knapp's Standard Mercuric Cyanide are described in Sutton's "Vol. Anal.," p. 311, and are used for the estimation of sugar. See also pp. 165, 281.

Nessler's Reagent, see p. 189.

Thoulet's Solution consists of a solution of mercuric iodide in potassium iodide; has a sp. gr. of 3·17, and is used for the separation of minerals.

Mayer's Solution, formed by dissolving 13·53 gms. mercuric chloride and 49·67 gms. potassium iodide in water at 15° and diluting to a litre, is a test for alkaloids.

MERCURIC OXIDE.—Hydrargyrum oxydatum (HgO). Mol. wt., 216·6. It may be obtained either as the moist yellow modification or as a red powder. Insoluble in water.

Tests for Impurities.—*Residue.*—2 gms. must leave no residue on ignition.

Chlorine and Sulphuric Acid.—A solution (1 : 100) in dilute nitric acid must give no reaction with either silver nitrate or barium chloride.

Nitric Acid.—On shaking 1 gm. with 2 c.c. of water, and then 2 c.c. of sulphuric acid, the addition of 1 c.c. ferrous sulphate solution must not show the characteristic reaction, even after standing a long time.

Uses and Storage.—The moist yellow form is used for the decomposition of magnesium chloride, and also, according to Meineke, for the precipitation of manganese. For this latter purpose absolute freedom from iron is essential, and it is better therefore to avoid using the red oxide. The pure oxide, free from nitrogen and sulphur, is used in the ultimate organic

analysis of substances containing these elements, and in the Kjeldahl process for estimation of nitrogen.

Commercial Varieties.—Both the red and yellow modifications leave a considerable residue on ignition; even in the purest samples there are nearly always unweighable traces of residue present.

MERCUROUS NITRATE.—Hydrargyrum nitric. oxydulat. pur. $Hg_2(NO_3)_2 . 2H_2O$. Mol. wt., 561·25. White monoclinic crystals soluble in water, but with a large quantity of water forms the basic salt.

Tests for Impurities.—*Volatility.*—2 gms. must leave no weighable residue on ignition in a porcelain crucible.

Mercuric Salt.—On dissolving 1 gm. in a small quantity of very dilute nitric acid, diluting to 20 c.c., and adding cold dilute hydrochloric acid in excess and filtering, the filtrate should only show traces of a precipitate with hydrogen sulphide.

Quantitative Estimation.—A number of methods are given for the analysis of mercurous compounds. The mercury in the nitrate may be estimated by precipitation as mercurous chloride.

Uses and Storage.—It is used as a test for easily oxidisable substances, such as formic acid, and is very poisonous. Mercurous nitrate may also be employed in testing for tungstates and molybdates with which it forms a green precipitate dissolved by KI and HCl yielding a blue colour (E. Kafka, "Zeits. für anal. Chem.," 1912, p. 483; Merck's "Annual," 1912, p. 277).

Commercial Varieties.—These often contain considerable quantities of the mercuric salt, and since on testing for this impurity the mercuric salt is liable to be formed, great care must be exercised.

META-DIAMIDO-BENZENE.— See "Meta-Phenylene-Diamine Hydrochloride".

META-PHENYLENE-DIAMINE. — Meta-diamido-benzol $C_6H_4(NH_2)_2$. Colourless or reddish crystals. M.p., 63°. Soluble in water and alcohol.

Uses.—Meta-phenylene-diamine is used as a test for salts of gold with which it produces a violet colour (J. A. Siemssen, "Chem. Zeit.," 1912, p. 943; Merck's "Index," 1912, p. 355). It has also been proposed by Storch as a test for distinguishing between unboiled and boiled milk (*ibid.*).

The hydrochloride ($C_6H_4(NH_2)_2 2HCl$) is also employed as a reagent in testing for nitric acid (Greiss) in the detection of nitric acid, hydrogen peroxide, ozone, aldehydes, ketones, and lignin (Merck's "Index," p. 285), see also below.

META-PHENYLENE-DIAMINE HYDROCHLORIDE ($C_6H_4(NH_2)_2$, 2HCl).—White or slightly reddish-white crystalline powder, easily soluble in water. M.p., 63°.

Tests for Impurities.—The reddish colour just mentioned owes its presence to the action of the atmosphere. The aqueous solution (1 : 20) should be either colourless or show only a faint yellow colour.

Uses and Storage.—The aqueous solution (1 : 200) gives a yellow or brown colour in solutions containing even traces of nitrites, after acidifying with sulphuric acid. A sharp reaction is also produced in presence of aldehyde, it is therefore employed for the detection of the latter in alcohol (see p. 10).

On its employment as a test for hydrogen peroxide see Denigés, "J.C.S.," 1891, p. 1549; and for the detection of free oxygen, see Cazeneuve, "J.S.C.I.," 1891, p. 796.

The salts of this compound have the disadvantage of being decomposed even in solution by the action of the atmosphere, and must on this account be kept in tightly-stoppered bottles. If a salt gives a highly coloured solution, animal charcoal must be added to decolorise it before it is used as a reagent; ammoniacal solutions decolorised in this way are said to keep very well. The reagent may also be prepared by dissolving 5 gms. of the purest meta-phenylene-diamine (melting at 63°) in dilute sulphuric acid until a distinct acid reaction is observed, and diluting to 1 litre with water. If the solution is coloured it is better to use animal charcoal which has been previously ignited in a closed crucible.

Note.—For the detection of free oxygen, we may mention two reagents, which have but a limited use compared with the above—

namely, the dimethyl and tetramethyl para-phenylene-diamine recommended by C. Wurster. For their preparation and properties, see "J.S.C.I.," 1887, p. 304; 1888, p. 404.

METHYLENE BLUE.—Tetramethylthionine hydrochloride ($C_{16}H_{18}N_3SCl + 3H_20$). Dark green powder with a bronze lustre, easily soluble in water to a blue solution; less soluble in alcohol.

Tests for Impurities.—*Arsenic.*—2 gms. are mixed with sodium carbonate and saltpetre, and after ignition, tested in Marsh's apparatus (see "Zinc").

Ash.—Only traces of residue must remain after igniting 2 gms. of the sample.

Note.—Full details regarding the tests to be applied are given by Lenz ("J.S.C.I.," 1895, p. 772).

Uses.—It is used as a bacteriological stain (see "Preparation of Reagents" in Appendix).

Also as a test for bile pigments by A. von Torday and A. Klier (Merck's "Annual," 1910, p. 260). F. S. Sinnat used methylene blue as an indicator in iodometry ("Analyst," 1910, p. 309). Béla v. Ondrejorich uses it as a test for aceto-acetic acid in urine ("Deut. med. Wochen.," 1912, p. 1413; Merck's "Annual," 1912, p. 289).

For the uses of methylene blue in analysis, see F. W. Atack ("J. Soc. Dyers and Col.," 1915, pp. 183-188, 203-208), A. Monnier ("Arch. Sci. phys. nat.," 1916, 42, pp. 21-216; "J.S.C.I.," 1917, p. 49).

Commercial Varieties.—A double salt of zinc and the base is sold under the name of methylene blue, but may readily be recognised on testing the ash for zinc. According to Lenz, the methylene blue sold is often very impure.

METHYL ORANGE.—Sodium dimethylamidoazobenzene sulphonate ($(SO_3Na)C_6H_4N_2C_6H_4N(CH_3)_2$). Orange-yellow scales, easily soluble in water.

Tests.—A 0·1 per cent. solution is made and tested against hydrochloric or sulphuric acid. Very little of the indicator must be added to the solution to be titrated—in fact, not more than is sufficient to impart a faint yellow colour. To perform the test, 100 c.c. distilled water are placed in a Jena glass

beaker, and the solution just coloured yellow with the indicator; on now adding 2 drops of $\frac{n}{5}$ acid the colour must deepen to a dark reddish-yellow. Comparative tests with this indicator are given on p. 141, and particularly below under "Uses".

Uses.—The above indicator, which was recommended by Lunge, has the great advantage of being unaffected by weak acids, such as carbonic, acetic, etc., and continued boiling of liquids containing CO_2 during titration is therefore rendered unnecessary. The indicator can only be used in the cold, and is useless for oxalic acid. On account of the above-mentioned advantage many prefer it to litmus, also for that reason it finds special favour with alkali makers in the analysis of soda ash. Many observers have tested its sensitiveness against litmus, and Reinitzer, for example, concludes from his comparative experiments that in the determination of sodium carbonate it is not possible to obtain such accurate results as with litmus ("J.C.S.," 1895, A., ii., p. 134). According to him, the change of colour, or end reaction, in titrating with acids, is not so sharp with methyl orange as with litmus, and he states that in his experiments the colour did not change quickly from light yellow to purple-red, but passed through gold brown or dark yellow to red with a yellowish-tint which, in litmus titrations, is termed onion-skin red. In contradistinction to this opinion Lunge ("Zeit. f. anal. Chem.," 1894, p. 733) considers its sensitiveness to be much greater than Reinitzer supposed, but states that the titration must not be continued until the appearance of a purple-red colour. When titrating with $\frac{n}{5}$ acid, the reaction must be regarded as complete at the first change of colour, namely, from light yellow to a dark orange-yellow (see Lunge, loc. cit.) The purity of the indicator is a matter of the greatest importance. Dott ("Zeit. f. anal. Chem.," 1890, p. 321) calls attention to the impurities present in commercial methyl orange, and emphasises the fact that the results vary according to the purity of the sample used. To obtain satisfactory results only the purest quality should be used. The Association of Swiss Analysts ("Chem.-Ztg.," 1895, p. 1895) employed the indicator in estimating the alkalinity of potable waters; for this delicate test many of the preparations on the market

are utterly useless. On the use of this indicator for the estimation of borates of the alkalies and alkaline earths, alkaline sulphides, direct estimation of alkaline carbonates, and also its reaction with alkaline sulphites, see Sutton's "Volumetric Analysis". A number of papers have appeared in the journals on this indicator, particularly the communications by R. T. Thomson ("Chem. News," vol. xlvii., pp. 123, 185; vol. xlix., pp. 32, 119; "J.S.C.I.," 6, p. 195); see also Lunge's "Manufacture of Sulphuric Acid". On the sensitiveness of indicators, see Lunge and Marmier ("J.C.S.," 1897, A., ii., pp. 285, 386).

Commercial Varieties.—See under "Uses".

METHYL SULPHATE.—Methyl sulphate 1 or 2 c.c. heated with a trace of colophony gives a rose coloration which changes to violet and then to deep violet. On further heating the colour is destroyed almost entirely, there remaining only a faint brown coloration. This reaction is stated to be more characteristic than that of Liebermann, while it is simpler than Halphen's test (J. Sans, "Ann. Chim. Analyt.," 1909, 14, pp. 140-141; "J.S.C.I.," 1909, p. 483).

METHYL VIOLET.—This colouring matter is composed chiefly of the hydrochlorides of pentamethyl-pararosaniline ($C_{24}H_{28}N_3Cl$) and the hexa-compound ($C_{25}H_{30}N_3Cl$). A blue powder, easily soluble in water and alcohol.

Tests.—As under "Methylene Blue".

Uses.—It is used as a stain, and has a highly destructive effect on bacteria (see E. Merck's "Annual Reports," 1891 to 1894). Also for detecting mineral acids in vinegar. It gives a blue or green colour if they are present.

Commercial Varieties.—The very pure compound is sold by E. Merck under the name "Pyoktanin".

MICROCOSMIC SALT.—See "Sodium Ammonium Phosphate".

MOLYBDENUM SOLUTION FOR PHOSPHORIC ACID ESTIMATION.—See p. 197.

MOLYBDIC ACID.—Acid molybdaenic. pur. (MoO_3). Mol wt., 144. White or slightly yellowish-white powder, or fine needles, slightly soluble in water (1 : 500).

Tests for Impurities.—*Solubility, Heavy Metals.*—The solution (1 : 5) in dilute ammonia must be clear, and show no precipitate with ammonium sulphide.

Phosphoric Acid.—On dissolving 10 gms. in 25 c.c. of water and 15 c.c. of ammonia, sp. gr. 0·910, and mixing this solution with 150 c.c. of nitric acid (1 : 20) no yellow precipitate must appear after standing at a gentle heat for 2 hours (ammonium phosphomolybdate; see also note under "Ammonium Molybdate").

Note.—Molybdic acid is used very considerably in chemical laboratories. König ("Rep. f. anal. Chem.," 84, No. 11, p. 161) records a number of comparative analyses of the commercial varieties.

Quantitative Estimation.—Pure molybdic acid, as well as ammonium molybdate, may be estimated gravimetrically by dissolving in ammonia, neutralising with acetic acid, and precipitating the boiling solution with slight excess of lead acetate; after filtering, the precipitate is washed with hot water and dried. It is then removed from the filter, ignited, and weighed as PbO, MoO_3 (see Fresenius, "Quant. Anal.," vol. i., p. 289). A volumetric method for its estimation is described in "Ber. d. d. Chem. Ges.," 1888, 3, p. 485. A paper by Friedheim and Euler ("J.C.S.," 1895, A., ii., p. 535) on its quantitative estimation may also be referred to. See also an article by Gooch and Fairbanks ("J.C.S.," 1897, A., ii., p. 76).

Uses.—Molybdic acid and ammonium molybdate are both used for the detection and estimation of phosphoric acid, the solutions being prepared in a special way. P. Wagner ("J.C.S.," 1896, A., p. 448) recommends the following methods: (*a*) 125 gms. molybdic acid are transferred to a litre flask shaken with about 100 c.c. of water, and the mixture dissolved in about 300 c.c. of 8 per cent. ammonia. To this solution 40 gms. of ammonium nitrate are added, and the solution made up to the mark with water. The contents of the flask are now mixed with a litre of nitric acid, 1·19 sp. gr., the mixture allowed to stand for 24 hours at about 35° C., and filtered. (*b*) 150 gms. ammonium molybdate are dissolved in water in a litre flask; to the solution 400 gms. ammonium nitrate are added, the flask filled up to the mark and mixed with a litre of nitric acid of the same strength as

above, and the mixture treated as at (*a*). A precipitate sometimes settles out on standing, which is not an impurity, but a yellow modification of molybdic acid (see note under "Ammonium Molybdate," p. 33).

Meineke ("Chem.-Ztg.," 1896, p. 108) recommends the following preparation: 150 gms. ammonium molybdate are dissolved in 150 c.c. ammonia, sp. gr. 0·910, and 850 c.c. of water; the mixture is then poured, whilst shaking, into a litre of nitric acid, sp. gr. 1·2. The solution is then heated for 10 minutes at 90°, and subsequently separated from the copious precipitate of molybdic acid by decantation and filtration. When kept in brown bottles and protected from the light, this solution remains clear for a long time, and can be used for the estimation of phosphoric acid without danger of further precipitation.

Frohde's Reagent.—This consists of a solution of pure molybdic acid in concentrated sulphuric acid, and is employed for the detection of alkaloids.

According to Denigés ("J.C.S.," 1891, A., p. 1549) the acid can be used as a test for hydrogen peroxide.

Remarks.—Molybdic acid among other uses is employed as a test for alcohol and as a colour test for various substances. According to E. Merck ("J.C.S.," 1897, A., ii., p. 164) the test for alcohol is conducted as follows :—

The acid is dissolved by heating with concentrated sulphuric acid, and the solution thus prepared is poured cautiously into a test tube containing the liquid to be tested until it forms a lower layer. During the test the temperature ought not to rise above 60°. At the juncture of the two liquids a distinct blue ring will appear, increasing in intensity according to the quantity of alcohol present. As little as 0·02 per cent. of ethyl alcohol and 0·2 per cent. of methyl alcohol may be detected by this method.

Commercial Varieties.—These consist of the "pure" and "puriss.," the latter being described in the following article. Commercial samples vary greatly regarding percentage of MoO_3 and the quantity of ammonium nitrate and salts of sodium they contain.

MOLYBDIC ACID, FREE FROM AMMONIA.—Acid. molybdænic. puriss. free from ammonia (MoO_3). Mol. wt., 144. The preparation contains nearly 100 per cent. MoO_3, but has a slight bluish shade owing to the presence of traces of molybdic oxide. The acid is almost insoluble in water.

Tests for Impurities.—*Solubility, Heavy Metals.*—2 gms. are dissolved in 10 c.c. of water and 5 c.c. of ammonia, sp. gr. 0·910; after standing for a short time at a gentle heat the solution must give no precipitate with excess of ammonium sulphide.

Phosphoric Acid.—As in the foregoing preparation.

Ammonium and Sodium Salts.—On extracting 2 gms. with water only traces of soluble substances should dissolve out.

Quantitative Estimation and Commercial Varieties.—See "Molybdic Acid," pure.

***a*-NAPHTHOL.**—Naphtholum (*a*) recryst. alb.: alpha-naphthol ($C_{10}H_7OH$). Mol. wt., 144·1. Colourless crystals, melting at 97°; have a phenolic odour; easily soluble in alcohol and ether, almost insoluble in water.

Tests for Impurities.—*Residue.*—On ignition of 1 gm. of the sample no residue must remain.

Other Impurities.—The crystals of pure naphthol ought to be colourless and show the above melting point.

Quantitative Estimation.—The purity of the preparation may be gauged from the above properties.

Uses.—The compound is used for Molisch's sugar test ("J.S.C.I.," 1887, p. 149), and on its practical application for this reaction see Posner and Epenstein, "Chem. Centralblatt," 1891, p. 641. It is also used for the detection of chloroform and chloral hydrate, for which purpose a few c.c. of naphthol-potash solution (0·1 : 50 gms.) are heated in a test tube, and the liquid to be tested added; in the presence of chloroform or chloral hydrate a permanent and intensely blue colour appears; when *β*-naphthol is employed the blue colour remains only a short time. This reaction presents a speedy method of distinguishing the naphthols, according to Reuter ("J.S.C.I.," 1891, p. 799). Also employed in detecting cotton in woollen stuffs.

Commercial Varieties.—A commercial product for technical purposes, consisting of fused crystalline lumps and always containing β-naphthol, may be obtained.

β-NAPHTHOL.—Beta naphthol may be employed for the detection of commercial invert sugar in honey. In presence of invert sugar after addition of sulphuric acid it yields a red to bluish-violet colour, whereas pure honey gives only a yellowish or reddish colour (F. M. Litterscheid, "Chem. Zeit.," 1913, 37, p. 321; "J.S.C.I.," 1913, p. 376).

β-NAPHTHOLBENZYLAMINE.—Formula

$$(C_{10}H_6 . OH) (C_6H_5) CH . NH_2.$$

Uses.—May be employed for distinguishing between aldoses with which it forms crystalline compounds and ketoses upon which it has no action (M. Betti, "Gaz. Chim. Ital.," 1912, 42, pp. 288-294).

NAPHTHOL CARBONIMIDE. — Naphthyl - isocyanide. Liquid boiling at 269°-270°.

This compound, which was first described by A. W. Hoffmann, was suggested by C. Neuberg as a reagent for the separation of amino acids, also for the identification of aliphatic alcohols with which it combines to form α-naphthyl-methanes which can be distinguished by their melting points ("Neuberg-Manasse. Ber.," 1905, p. 2359: Merck's "Annual," 1909, p. 265).

β-NAPHTHO-QUINONE-A-OXIME.—The sodium salt of this oxime is recommended by F. W. Atack, "J.S.C.I.," 1915, 641) as a far more delicate test for Co than nitroso β-naphthol. The reagent is prepared by dissolving 0·1 gm. of the oxime in 20 c.c. of boiling water, adding 1 c.c. dilute solution of sodium hydrate and making up to 200 c.c. 1 c.c. ammonium chloride solution and 1 c c. of the reagent are added to the solution to be tested which should be neutral or slightly alkaline when in presence of cobalt an orange-claret coloration or precipitate is formed, unaffected by sulphuric acid. 1 pt. of cobalt in 1 million of water can thus be detected The reagent gives colorations with nickel and ferrous salts,

etc., but these are destroyed with sulphuric acid. No coloration is obtained with zinc or manganese salts. The cobalt must be in the cobaltous state and the coloration is not affected by moderate amounts of nickel, although large quantities of the latter metal affect it.

α-NAPHTHYLAMINE HYDROCHLORIDE.—Formula $C_{10}H_7NH_2HCl$. Mol. wt., 179·6. White crystalline powder with a grey tint. It has a peculiar odour not unlike that of faeces. Slightly soluble in water.

Uses.—It is employed along with sulphanilic acid and dilute hydrochloric acid as a very delicate test for nitrites with which it gives a pink colour deepening considerably on standing.

The salt gradually decomposes on standing, becoming greyer and insoluble in water.

Note.—Naphthylamine sulphonic acid, $2C_{10}H_6(NH_2)SO_3H[1:4] + H_2O$, is used for the same purpose.

α-Naphthylamine gives an intense blue colour with chromates in presence of tartaric, citric, or oxalic acid. 0·001 m. gram. of chromium can thus be detected (P. N. van Eck., "Chem. Weekblad.," 1915, 12, pp. 6-8; "Analyst," 1915, 40, p. 292).

NESSLER'S REAGENT.—See "Mercuric Chloride," p. 189.

NITRIC ACID.—Acidum nitricum purum (HNO_3). Mol. wt., 63·02. Clear, colourless liquid. Sp. gr., 1·2. Containing about 33 per cent. HNO_3.

Tests for Impurities.—*Residue.*—10 gms. must leave no weighable residue on evaporation in a platinum capsule.

Note.—Hempel and Thiele ("Zeit. f. anorg. Chem.," 1896, p. 78) have published some articles on the subject of residual matter in the pure acid. According to these authors, 60 c.c. ought only to leave a residue of 0·0013 gm., equal to 0·0015 per cent., on evaporation. A smaller quantity of residue was obtained after distilling the acid in a flask into which was ground a hollow stopper terminating in a tube bent over into a platinum condenser; by using these precautions, a residue of 0·00041 gm., or 0·0003 per cent. was obtained on treating 140 gms. of the sample. This acid was specially prepared for atomic weight determinations.[1]

[1] Hempel and Thiele also prepared other reagents, such as ammonium chloride and ammonium sulphide, for the same purpose, but

Sulphuric Acid.—10 gms. are evaporated in a porcelain basin to about half a c.c. diluted with 30 c.c. of water, transferred to a beaker, heated, and tested with barium chloride; no precipitate must form even after long standing.

Note.—As already mentioned under "Hydrochloric Acid, pure" (p. 124), the acids, particularly nitric, interfere to some extent with the test for sulphuric acid. The further, therefore, the evaporation of the nitric acid is carried, the more certain the reaction.

Chloride.—50 c.c. of distilled water, to which a few drops of silver nitrate have been added, must show no reaction with 5 c.c. to 10 c.c. of nitric acid.

Note.—The silver nitrate is added first as a safeguard against the possible presence of chlorine in the water.

Heavy Metals and Earths.—20 gms. of the acid are diluted with water, ammonia added in excess, and subsequently ammonium sulphide and ammonium oxalate; no dark colour or turbidity must appear.

Iodine.—As little as 0·005 per cent. of iodine imparts a yellow colour to the acid; this colour may also be due to chlorine compounds, but is generally caused by the presence of hyponitric acid. Iodine may be detected by shaking with chloroform (Biltz), but it is not usually present in the free state. On adding carefully a very dilute solution of sulphurous acid or a few drops of hydrogen sulphide water, the iodine, whether present as an oxygen compound or in the free state, can then be detected by carbon disulphide or starch solution. The reaction is spoiled, however, if an excess of either reagent is used. The committee of the Society of German Pharmacists give the following practical tests for iodine or iodic acid: On shaking the acid, diluted with twice its volume of water, with a little chloroform the latter must not assume a violet colour, even after introducing a piece of metallic zinc, which must be in contact with the acid ("Arch. f. Pharm.," 1887, p. 93).

Hyponitric Acid, etc.—The test is made with permanganate solution (see p. 210). Absolute freedom from the lower oxides

none could be obtained entirely free from residue on ignition. The chloride gave a very minute trace on ignition on platinum foil; the sulphide showed 0·0065 per cent. on evaporation.

of nitrogen is at once shown by the dilute solution retaining the red colour produced by the first drop of deci-normal permanganate solution. Hyponitric acid is nearly always present, however, especially in the strong acid (see also "Uses").

Quantitative Estimation.—The percentage may be found either from the specific gravity, taken by Mohr's balance, or by titration with normal alkali, using litmus as indicator.

Note.—The titration of the strong acid, containing nitrous acid, is rendered very difficult in consequence of the fumes evolved, but where such an estimation is necessary, the method recommended by Lunge and Marchlewski ("J.S.C.I.," 1892, p. 432) had better be adopted. These authors run 10 c.c. of the acid, drop by drop, from a narrow and accurately standardised burette, into a little ice-cold water, dilute to 100 c.c., and titrate an aliquot portion of the solution with standard soda.

For table showing the strength of nitric acid of various specific gravities at 15°, compared with water at 4°, by Lunge and Rey, see pp. 204-209.

Uses and Storage and Normal Nitric Acid.—The acid is used as an oxidising agent and for the nitration of organic compounds. It dissolves many of the metals with evolution of nitric oxide. The acid is employed in very varying degrees of concentration, according to the purpose for which it is required. The red fuming acid, also used for analytical purposes, is a solution of hyponitric acid in concentrated nitric acid. The ordinary pure acid is often used for the oxidation of sulphur and sulphides to sulphuric acid, and for the analysis of organic compounds, and must be free from sulphuric acid. It is also used in the quantitative estimation of chlorine, bromine, and iodine in organic compounds. A fairly concentrated acid free from hyponitric acid may be obtained by passing air through it while heating on the water bath, but acids of the higher concentrations cannot be so readily freed from this impurity, as they have a tendency to decompose into hyponitric acid, oxygen, and water. Lunge and Rey ("J.S.C.I.," 1891, p. 543) purified such acids by means of sulphuric monohydrate.

The acid should be kept in a cool place, and in glass stoppered bottles. Accidents have often occurred through careless manipulation and storage (see "Chem. Industrie," 1899, p. 441;

SPECIFIC GRAVITIES OF NITRIC ACIDS AT
(LUNGE

Sp. Gr. at $\frac{15°}{4°}$ (in Vacuo).	°B.	°Tw.	100 Parts by Weight Contain				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·000	0	0	0·08	0·10	0·19	0·16	0·10
1·005	0·7	1	0·85	1·00	1·89	1·61	1·03
1·010	1·4	2	1·62	1·90	3·60	3·07	1·95
1·015	2·1	3	2·39	2·80	5·30	4·52	2·87
1·020	2·7	4	3·17	3·70	7·01	5·98	3·79
1·025	3·4	5	3·94	4·60	8·71	7·43	4·72
1·030	4·1	6	4·71	5·50	10·42	8·88	5·64
1·035	4·7	7	5·47	6·38	12·08	10·30	6·54
1·040	5·4	8	6·22	7·26	13·75	11·72	7·45
1·045	6·0	9	6·97	8·13	15·40	13·13	8·34
1·050	6·7	10	7·71	8·99	17·03	14·52	9·22
1·055	7·4	11	8·43	9·84	18·64	15·89	10·09
1·060	8·0	12	9·15	10·68	20·23	17·25	10·95
1·065	8·7	13	9·87	11·51	21·80	18·59	11·81
1·070	9·4	14	10·57	12·33	23·35	19·91	12·65
1·075	10·0	15	11·27	13·15	24·91	21·24	13·49
1·080	10·6	16	11·96	13·95	26·42	22·53	14·31
1·085	11·2	17	12·64	14·74	27·92	23·80	15·12
1·090	11·9	18	13·31	15·53	29·41	25·08	15·93
1·095	12·4	19	13·99	16·32	30·91	26·35	16·74
1·100	13·0	20	14·67	17·11	32·41	27·63	17·55
1·105	13·6	21	15·34	17·89	33·89	28·89	18·35
1·110	14·2	22	16·00	18·67	35·36	30·15	19·15
1·115	14·9	23	16·67	19·45	36·84	31·41	19·95
1·120	15·4	24	17·34	20·23	38·31	32·67	20·75
1·125	16·0	25	18·00	21·00	39·77	33·91	21·54
1·130	16·5	26	18·66	21·77	41·23	35·16	22·33
1·135	17·1	27	19·32	22·54	42·69	36·40	23·12
1·140	17·7	28	19·98	23·31	44·15	37·65	23·91
1·145	18·3	29	20·64	24·08	45·61	38·89	24·70
1·150	18·8	30	21·29	24·84	47·05	40·12	25·48
1·155	19·3	31	21·94	25·60	48·49	41·35	26·20
1·160	19·8	32	22·60	26·36	49.92	42·57	27·04
1·165	20·3	33	23·25	27·12	51·36	43·80	27·82
1·170	20·9	34	23·90	27·88	52·80	45·03	28·59
1·175	21·4	35	24·54	28·63	54·22	46·24	29·36
1 180	22·0	36	25·18	29·38	55·64	47·45	30·13
1·185	22·5	37	25·83	30·13	57·07	48·66	30·90
1·190	23·0	38	26·47	30·88	58·49	49·87	31·67
1·195	23·5	39	27·10	31·62	59·89	51·07	32·43
1·200	24·0	40	27·74	32·36	61·29	52·26	33·19
1·205	24·5	41	28·36	33·09	62·67	53·23	33·94
1·210	25·0	42	28·99	33·82	64·05	54·21	34·69
1·215	25·5	43	29·61	34·55	65·44	55·18	35·44
1·220	26·0	44	30·24	35·28	66·82	56·16	36·18
1·225	26·4	45	30·88	36·03	68·24	57·64	36·95
1·230	26·9	46	31·53	36·78	69·66	59·13	37·72
1·235	27·4	47	32·17	37·53	71·08	60·61	38·49

15° C. (Compared with Water at 4°).
and Rey.)

1 Litre Contains Kgms.				
N_2O_5.	HNO_3.	Acid of 36° B	Acid of 40° B.	Acid of 48½° B.
0·001	0·001	0·002	0·002	0·001
0·008	0·010	0·019	0·016	0·010
0·016	0·019	0·036	0·031	0·019
0·024	0·028	0·053	0·045	0·029
0·033	0·038	0·072	0·061	0·039
0·040	0·047	0·089	0·076	0·048
0·049	0·057	0·108	0·092	0·058
0·057	0·066	0·125	0·107	0·068
0·064	0·075	0·142	0·121	0·077
0·073	0·085	0·161	0·137	0·087
0·081	0·094	0·178	0·152	0·096
0·089	0·104	0·197	0·168	0·107
0·097	0·113	0·214	0·182	0·116
0·105	0·123	0·233	0·198	0·126
0·113	0·132	0·250	0·213	0·135
0·121	0·141	0·267	0·228	0·145
0·129	0·151	0·286	0·244	0·155
0·137	0·160	0·303	0·258	0·164
0·145	0·169	0·320	0 273	0·173
0·153	0·179	0·339	0·289	0·184
0·161	0·188	0·356	0·304	0·193
0·170	0·198	0·375	0·320	0·203
0·177	0·207	0·392	0·335	0·212
0·186	0·217	0·411	0·350	0·223
0·195	0·227	0·430	0·366	0·233
0·202	0·236	0·447	0·381	0·242
0·211	0·246	0·466	0·397	0·252
0·219	0·256	0·485	0·413	0·263
0·228	0·266	0·504	0·430	0·273
0·237	0·276	0·523	0·446	0·283
0·245	0·286	0·542	0 462	0·293
0·254	0·296	0·561	0·478	0·304
0·262	0·306	0·580	0·494	0·314
0·271	0·316	0·598	0·510	0·324
0·279	0·326	0·617	0·526	0·334
0·288	0·336	0·636	0·543	0·345
0·297	0 347	0·657	0·560	0·356
0·306	0·357	0 676	0·577	0·366
0·315	0·367	0·695	0·593	0·376
0·324	0·378	0·715	0·610	0·388
0·333	0·388	0·735	0·627	0·398
0·342	0·399	0·755	0·644	0·409
0·351	0·409	0·775	0·661	0·419
0·360	0·420	0·795	0·678	0·431
0·369	0·430	0·815	0·695	0·441
0·378	0·441	0·835	0·712	0·452
0·387	0·452	0·856	0·730	0·466
0·397	0·463	0·877	0·748	0·475

SPECIFIC GRAVITIES OF NITRIC ACIDS AT
(LUNGE

Sp. Gr at $\frac{15°}{4°}$ (in Vacuo).	°B.	°Tw.	100 Parts by Weight Contain				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·240	27·9	48	32·82	38·29	72·52	61·84	39·27
1·245	28·4	49	33·47	39·05	73·96	63·07	40·05
1·250	28·8	50	34·13	39·82	75 42	64·31	40·84
1·255	29·3	51	34·78	40·58	76·86	65·54	41·62
1·260	29·7	52	35·44	41·34	78·30	66·76	42·40
1·265	30·2	53	36·09	42·10	79·74	67·99	43·18
1·270	30·6	54	36·75	42·87	81·20	69·23	43·97
1·275	31·1	55	37·41	43·64	82·65	70·48	44·76
1·280	31·5	56	38·07	44·41	84·11	71·72	45·55
1·285	32·0	57	38·73	45·18	85·57	72·96	46·34
1·290	32·4	58	39·39	45·95	87·03	74·21	47·13
1·295	32·8	59	40·05	46·72	88·48	75·45	47·92
1·300	33·3	60	40 71	47·49	89·94	76 70	48·71
1·305	33·7	61	41·37	48·26	91·40	77·94	49·50
1·310	34·2	62	42·06	49·07	92·94	79·25	50·33
1·315	34·6	63	42·76	49·89	94·49	80·57	51·17
1·320	35·0	64	43·47	50·71	96·05	81·90	52·01
1·325	35·4	65	44·17	51·53	97·60	83·22	52·85
1·330	35·8	66	44 89	52·37	99·19	84·58	53·71
1·3325	36·0	66·5	45·26	52·80	100·00	85·27	54·15
1·335	36·2	67	45·62	53·22	100·80	85·95	54·58
1·340	36·6	68	46·35	54·07	102·41	87·32	55·46
1·345	37·0	69	47·08	54·93	104·04	88·71	56·34
1·350	37·4	70	47·82	55·79	105·67	90 10	57·22
1·355	37·8	71	48·57	56·66	107·31	91·51	58·11
1·360	38·2	72	49·35	57·57	109·03	92·97	59·05
1·365	38·6	73	50·13	58·48	110·75	94·44	59·98
1·370	39·0	74	50·91	59·39	112·48	95·91	60·91
1·375	39·4	75	51·69	60·30	114·20	97·38	61·85
1·380	39·8	76	52·52	61·27	116·04	98·95	62·84
1·3833	40·0	—	53 08	61·92	117 27	100·00	63·51
1·385	40·1	77	53·35	62·24	117·88	100 51	63·84
1·390	40·5	78	54·20	63·23	119·75	102·12	64·85
1·395	40·8	79	55·07	64·25	121·68	103·76	65·90
1·400	41 2	80	55·97	65·30	123·67	105·46	66·97
1·405	41·6	81	56·92	66·40	125·75	107·24	68·10
1·410	42·0	82	57·86	67·50	127·84	109·01	69·23
1·415	42·3	83	58·83	68 63	129·98	110·84	70·39
1·420	42·7	84	59·83	69·80	132·19	112 73	71·59
1·425	43·1	85	60·84	70·98	134·43	114·63	72·80
1·430	43·4	86	61·86	72·17	136·68	116·55	74·02
1·435	43·8	87	62·91	73·39	138·99	118·52	75·27
1·440	44·1	88	64·01	74·68	141·44	120·61	76·59
1·445	44·4	89	65·13	75·98	143·90	122·71	77·93
1·450	44 8	90	66·24	77·28	146·36	124·81	79·26
1·455	45·1	91	67·38	78·60	148·86	126·94	80·62
1·460	45·4	92	68·56	79·98	151·47	129 17	82·03
1·465	45·8	93	69·79	81·42	154·20	131·49	83·51
1·470	46·1	94	71·06	82·90	157·00	133·88	85·03
1·475	46·4	95	72·39	84·45	159·94	136·39	86·62

15° (Compared with Water at 4°).
and Rey.)

1 Litre Contains Kgms.				
N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
0·407	0·475	0·900	0·767	0·487
0·417	0·486	0·921	0·785	0·498
0·427	0·498	0·943	0·804	0·511
0·437	0·509	0·965	0·822	0·522
0·447	0·521	0·987	0·841	0·534
0·457	0·533	1·009	0·860	0·547
0·467	0·544	1·031	0·879	0·558
0·477	0·556	1·054	0·898	0·570
0·487	0·568	1·077	0·918	0·583
0·498	0·581	1·100	0·938	0·596
0·508	0·593	1·123	0·957	0·608
0·519	0·605	1·146	0·977	0·621
0·529	0·617	1·169	0·997	0·633
0·540	0·630	1·193	1·017	0·646
0·551	0·643	1·218	1·038	0·659
0·562	0·656	1·243	1·059	0·673
0·573	0·669	1·268	1·080	0·686
0·585	0·683	1·294	1·103	0·701
0·597	0·697	1·320	1·126	0·715
0·603	0·704	1·333	1·137	0·722
0·609	0·710	1·346	1·148	0·728
0·621	0·725	1·373	1·171	0 744
0·633	0·739	1·400	1·193	0·758
0·645	0·753	1·427	1·216	0·772
0·658	0·768	1·455	1·240	0·788
0·671	0·783	1·483	1·265	0·803
0·684	0·798	1·513	1·289	0·818
0·698	0·814	1·543	1·314	0·835
0·711	0·829	1·573	1·339	0·850
0·725	0·846	1·603	1·366	0·868
0·735	0·857	1·623	1·383	0·879
0·739	0·862	1·633	1·392	0·884
0·753	0·879	1·665	1·420	0·902
0·768	0·896	1·697	1·447	0 919
0·783	0·914	1·731	1·476	0·937
0·800	0·933	1·767	1·507	0·957
0·816	0·952	1·803	1·537	0·976
0·832	0·971	1·839	1·568	0·996
0·849	0·991	1·877	1·600	1·016
0·867	1·011	1·915	1·633	1·037
0·885	1·032	1·955	1·667	1·058
0·903	1·053	1·995	1·701	1·080
0 921	1·075	2·037	1·736	1·103
0·941	1·098	2·080	1·773	1·126
0·961	1·121	2·123	1·810	1·150
0·981	1·144	2·167	1·848	1·173
1·001	1·168	2·212	1·886	1·198
1·023	1·193	2·259	1·927	1·224
1·045	1·219	2·309	1·969	1·250
1·068	1·246	2·360	2·012	1·278

Specific Gravities of Nitric Acids at

(Lunge

Sp. Gr. at $\frac{15°}{4°}$ (in Vacuo).	°B.	°Tw.	100 Parts by Weight Contains				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B	Acid of 48½° B.
1·480	46·8	96	73·76	86·05	162·97	138·97	88·26
1·485	47·1	97	75·18	87·70	166·09	141·63	89·95
1·490	47·4	98	76·80	89·60	169·69	144·70	91·90
1·495	47·8	99	78·52	91·60	173·48	147·93	93·95
1·500	48·1	100	80·65	94·09	178·19	151·99	96·50
1·501			81·09	94·60	179·16	152·78	97·03
1·502			81·50	95·08	180·07	153·55	97·52
1·503			81·91	95·55	180·96	154·31	98·00
1·504			82·29	96·00	181·81	155·04	98·46
1·505	48·4	101	82·63	96·39	182·55	155·67	98·86
1·506			82·94	96·76	183·25	156·27	99·27
1·507			83·26	97·13	183·95	156·86	99·62
1·508	48·5		83·58	97·50	184·65	157·47	100·00
1·509			83·87	97·84	185·30	158·01	100·35
1·510	48·7	102	84·09	98·10	185·79	158·43	100·62
1·511			84·28	98·32	186 21	158·79	100·84
1·512			84·46	98·53	186·61	159·13	101·06
1·513			84·63	98·73	186·98	159·45	101·26
1·514			84·78	98·90	187·30	159·72	101·44
1·515	49·0	103	84·92	99·07	187·63	160·00	101·61
1·516			85·04	99·21	187·89	160·22	101·75
1·517			85·15	99·34	188·14	160·43	101·89
1·518			85·26	99·46	188·37	160·63	102·01
1·519			85·35	99·57	188·58	160·81	102·12
1·520	49·4	104	85·44	99·67	188·77	160·97	102·23

and "Zeit. f. angew. Chem.," 1897, 72, pp. 492-504: 1896, p. 675 *et seq.*).

Normal Nitric Acid.—The solution must contain 63·02 gms. HNO_3 per litre.[1] The amount of acid necessary, calculated roughly from the specific gravity, is weighed out and made up to the litre with water; the solution may then be standardised on transparent Iceland spar,[2] or by evaporation with ammonia, which is also a very accurate method (see "Zeit. f. anal. Chem.," 1893, p. 450; also p. 129 in this book).

[1] See also note under "Normal Caustic Potash," p. 257.

[2] On this method, using litmus as indicator, see Reinitzer, "Zeit. f. angew. Chem.," 1894, p. 551.

15° (Compared with Water at 4°).

and Rey.)

1 Litre Contains Kgms.				
N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·092	1·274	2·413	2·058	1·307
1·116	1·302	2·466	2·103	1·335
1·144	1·335	2·528	2·156	1·369
1·174	1·369	2·593	2·211	1·404
1·210	1·411	2·672	2·278	1·447
1·217	1·420	2·689	2·293	1·456
1·224	1·428	2·704	2·306	1·465
1·231	1·436	2·720	2·319	1·473
1·238	1·444	2·735	2·332	1·481
1·244	1·451	2·748	2·343	1·488
1·249	1·457	2·759	2·353	1·494
1·255	1·464	2·773	2·364	1·502
1·260	1·470	2·784	2·374	1·508
1·265	1·476	2·795	2·384	1·514
1·270	1·481	2·805	2·392	1·519
1·274	1·486	2·814	2·400	1·524
1·277	1·490	2·822	2·406	1·528
1·280	1·494	2·829	2·413	1·532
1·283	1·497	2·835	2·418	1·535
1·287	1·501	2·843	2·424	1·539
1·289	1·504	2·848	2·429	1·543
1·292	1·507	2·854	2·434	1·546
1·294	1·510	2·860	2·439	1·549
1·296	1·512	2·864	2·442	1·551
1·299	1·515	2·869	2·447	1·554

Commercial Varieties.—The "puriss." acid is sold of various strengths, as is also the pure fuming acid described in the following article.

NITRIC ACID, FUMING.—Acid. nitric. fumans pur. A solution of hyponitric acid in nitric acid. Reddish-yellow to reddish-brown liquid. Sp. gr., 1·48.

Tests for Impurities.—As in the preceding article.

Quantitative Estimation.—The specific gravity is used to describe the strength of the commercial acid. According to Krant, an acid of 1·518 sp. gr. contains 4·16 per cent. hyponitric acid. A large percentage of the latter is evidenced from the quantity and dark colour of the fumes which escape on

opening the bottle. According to Mohr ("Lehrbuch der Titrirmethode") the acid contains 4·2 per cent. hyponitric, and he estimates this by mixing the sample with water, using special precautions to ensure the conversion of hyponitric into nitrous and nitric acids, the former of which he estimates with permanganate. The red fuming acid contains varying proportions of nitric, nitrous, and hyponitric acids, but evidently the darker acid contains very little nitrous, if any. The usual test will not show this, as both these lower acids act similarly towards permanganate. On the titration with permanganate, see below.

Uses and Storage.—See "Nitric Acid," puriss.

Commercial Varieties.—These consist of the puriss. fuming, sp. gr., 1·525; and the pure, sp. gr., 1·48, according to the German Pharmacopœia. Like the pure they often contain sulphuric acid, therefore it is important to test for this impurity where the acid has to be used for the ultimate organic analysis of compounds containing sulphur.

NITRIC ACID, CRUDE.—A liquid, frequently very yellow in colour, owing to the presence of hyponitric acid. It often shows strong chlorine and sulphuric acid reactions, contains iron, and in many cases arsenic and iodic acid. The percentage of crude nitric acid from the specific gravity may be found in the tables on p. 204, *et seq.*

Note on Table.—It must be borne in mind that, in determining the specific gravity of nitric acid, particularly the crude acid, the lower oxides of nitrogen are generally present in such quantity as to seriously vitiate the results obtained. Lunge and Marchlewski ("J.S.C.I.," 1892, p. 432) recommend, therefore, that, in addition to estimating the percentage of real acid present by means of the specific gravity and titration with alkali, a quantitative determination of the hyponitric acid must also be made with standard permanganate, as follows: A narrow burette, accurately calibrated and divided into twentieths of a c.c. in order that 0·01 c.c. can be easily read off, is filled with the acid, which is then added drop by drop to a known quantity of seminormal permanganate solution, heated to 40°, till the colour disappears. The acid is allowed to stand in the burette for some time until it has attained the temperature of the room. The number of c.c. multiplied by the specific gravity corrected for temperature gives the weight of acid used, and the amount of N_2O_4 present is

Correction for the Specific Gravity of Nitric Acid containing Hyponitric Acid (Lunge and Marchlewski).

In the case of acids of sp. gr. 1·49 at $\frac{15^\circ}{4^\circ}$ the following deductions must be made to find the gravity equivalent to the nitric acid actually present :—

N_2O_4 Per Cent.	Correction.	N_2O_4. Per Cent.	Correction.	N_2O_4. Per Cent.	Correction.
0·25	0·0005	4·50	0·0288	8·75	0·0583
0·50	0·0008	4·75	0·0305	9·00	0·0600
0·75	0·0015	5·00	0·0323	9·25	0·0616
1·00	0·0030	5·25	0·0337	9·50	0·0633
1·25	0·0048	5·50	0·0360	9·75	0·0650
1·50	0·0068	5·75	0·0378	10·00	0·0660
1·75	0·0078	6·00	0·0395	10·25	0.0682
2·00	0·0105	6·25	0·0418	10·50	0·0698
2·25	0·0125	6·50	0·0430	10·75	0·0714
2·50	0·0143	6·75	0·0448	11·00	0·0730
2·75	0·0163	7·00	0·0465	11·25	0·0745
3·00	0·0180	7·25	0·0472	11·50	0·0760
3·25	0·0199	7·50	0·0500	11·75	0·0775
3·50	0·0217	7·75	0·0517	12·00	0·0785
3·75	0·0235	8·00	0·0533	12·25	0·0805
4·00	0·0253	8·25	0·0550	12·50	0·0820
4·25	0·0269	8·50	0·0566	12·75	0·0835

calculated from it. The permanganate may be standardised on iron, or with hydrogen peroxide in the nitrometer. The authors have analysed the strong commercial acid, sp. gr. 1·4960 at $\frac{5^\circ}{0^\circ}$ by this method, and also samples to which varying proportions of pure hyponitric acid had been added,[1] with the result that they have compiled the above table, which only necessitates an estimation of the hyponitric acid in order to find the correction to be made on the specific gravity; reference to the table of Lunge and Rey will then show the percentage of real acid present. This correction holds good where the hyponitric acid present is regarded as being inactive ; whereas if, as sometimes occurs, half the quantity is assumed to be in the active state, according to the formula—$N_2O_4 + H_2O = HNO_3 + HNO_2$, the above table cannot be used. The table is of great assistance, for example, in finding the strength of the strong acids used for nitrating purposes, where the whole of the N_2O_4 is regarded as inactive. Lunge has endeavoured to compile similar tables for stronger and weaker acids than those given, but could not obtain serviceable results ; he concludes that the total acid

[1] A detailed account of the results obtained is given in the reference quoted.

must be estimated by titration, and the hyponitric by permanganate, in order to find the influence exerted by the latter on the specific gravity ("J.S.C.I.," 1892, p. 775).

o-NITROBENZALDEHYDE, $C_6H_4\begin{cases}COH\\NO_2\end{cases}$. Mol. wt., 151·08. Light yellow needles, melting at 44°, and easily soluble in alcohol and ether. E. Lüdy employs an alcoholic solution of this compound for the detection of urea ("J.C.S.," 1889, A., p. 1059).

NITRON, $C_{20}H_{16}N_4$.

Busch ("J.S.C.I.," 1905, pp. 289, 638) made the important discovery that the endo-iminotriazoles formed compounds with nitric acid which were only sparingly soluble in water. The least soluble nitrate is that of 1 : 4 diphenyl 3 : 5 endo-anilo 4 : 5 dihydro-1 : 2 : 4 triazole which has been named "nitron". One molecule of this base combines with 1 molecule of nitric acid to form the compound $C_{20}H_{16}N_4 . HNO_3$. The delicacy of the reaction is such that 1 part of HNO_3 in 80,000 pts. of water can be detected (A. Chaston Chapman, "Proc. Chem. Soc.," 1917, p. 211; Merck's "Annual," 1909, p. 271).

Nitron also forms an insoluble picrate and may therefore be employed for the estimation of picric acid.

Note.—On the action of nitron on the various substances used in explosives, see J. Barab ("J. Amer. Chem. Soc.," 1917, pp. 504-514).

NITRO-PHENOL ($C_6H_4(OH)NO_2$). Mol. wt., 139·08. Orthonitrophenol consists of yellow needles, melting at 45°; those of the para compound are colourless and melt at 114°.

C.W. Teeter recommends nitro-phenol as a test for potassium ("Amer. Drugg.," 1887, 16, p. 81). According to Langbeck, it may be employed as a delicate indicator in alkalimetry ("Chem. Centralblatt," 1881, p. 387).

NITROPHENYLPROPIOLIC ACID.—Orthonitrophenylpropiolic acid, $C_6H_4(NO_2)C \equiv C . COOH$.

The acid, together with sodium carbonate or the sodium salt of the acid is employed as a test for sugar in urine. In the presence of glucose an indigo blue colour or precipitate is formed.

NITROSO-β-NAPHTHOL ($C_{10}H_6(NO)OH$). Mol. wt., 173·11. Orange-brown crystals, melting at 109·5°, sparingly soluble in water, and easily soluble in ether and hot alcohol.

The compound is used in quantitative analysis for the separation of metals, e.g., nickel and cobalt, etc. (G. v. Knorre, "J.S.C.I.," 1887, p. 384; 1893, p. 711; "Chem.-Ztg.," 1895, p. 1421).

OIL OF CLOVES.—See "Eugenol," p. 108.

ORCIN.—Methylresorcin Dihydroxytoluene,

$$C_6H_3(CH_3)(OH)_2 + H_2O.$$

White crystals. M.p., 60°, when free from water, 106°. Aromatic odour and sweet taste. When anhydrous, has a boiling point of 290°.

Uses.—Was recommended by F. Blumenthal as a test for pentoses in urine ("Med. Klinik," 1910, p. 550; Merck's "Annual," 1910, p. 261). A solution of orcin in concentrated hydrochloric acid containing ferric chloride is also used for the same purpose and is known as Bial's reagent (A. Jolles, "Zent. für innere Med.," 1912, p. 693; Merck's "Annual," 1912, p. 314).

OSMIC ACID. — Hyperosmic acid. Osmium tetroxide, OsO_4. Mol. wt., 254·9. Transparent yellow shining crystals which may be moulded in the hand. Soluble in about 50 parts of water.

Uses.—A 1 per cent. solution is employed for microscopical purposes for hardening and staining tissue. It imparts a deep black colour to many cells, fat, etc.

OXALIC ACID. — Acid. oxalic. puriss. ($C_2H_2O_4$, $2H_2O$). Mol. wt., 126·06. Colourless monoclinic crystals, which must show no sign of efflorescence. M.p., 98°-100°. Soluble in water (1 : 10).

Tests for Impurities.—*Residue.*—3 gms. must leave no residue on ignition in a platinum capsule.

Note.—Samples are often found containing potash, and leaving a strongly alkaline residue on ignition. The author lately examined three such samples marked "puriss." and found them to contain from

0·5 to 1 per cent. of potash; as the acid is used for potash estimations, this point is very important.

Sulphuric Acid.—5 gms. are dissolved in 100 c.c. of water and a few drops of hydrochloric acid and barium chloride added; after standing for several hours in a hot place no precipitate must form.

Heavy Metals.—The solution (1 : 10) must give no reaction with ammonia and ammonium sulphide and the solution must be clear.

Ammonia.—(*a*) On heating 2 gms. in a test tube with excess of caustic soda solution there must be no smell of ammonia and no reaction with moist turmeric paper. (*b*) 2 gms. are dissolved in 30 c.c. of water and excess of caustic potash (pure by alcohol) and 15 drops of Nessler's reagent added; no distinctly yellow or brownish-red colour should appear.

Note.—Samples containing a large quantity of ammonia, and causing serious discrepancies when used for the preparation of standard solutions, have been met with. An estimation of the acid present ought to show from 99 to 100 per cent. The crystals generally contain a small quantity of extraneous water, but are otherwise very pure, and may be used for all ordinary analytical purposes, i.e. for precipitating and separating purposes in qualitative and quantitative analysis. When the acid has to be used as a standard in alkalimetry, a sample showing exactly 100 per cent. must be used. This may be prepared by careful drying—a matter of great difficulty when large quantities are being treated.

Quantitative Estimation.—The acid may be estimated by titration with normal alkali (1 c.c. equals 0·06303 gm. $C_2H_2O_4$, $2H_2O$), or by standard permanganate solution. In the latter method 1 gm. is dissolved in 250 c.c. of water, 50 c.c. are drawn off, transferred to a beaker, and diluted with about 100 c.c. of water to which from 6 to 8 c.c. of pure concentrated sulphuric acid have been added; the mixture is then heated to about 60° C. The beaker is now placed on a white surface and permanganate added drop by drop from a burette, with constant stirring, until the red colour remains. The titre of the permanganate solution, which contains about 5 gms. per litre, is previously established on carefully dried oxalic acid (see "Uses") prepared as described above; a better method,

however, is to use potassium tetroxalate as the standard, see p. 276.

Uses, Storage, and Normal Oxalic Acid.—The pure acid is often used for standardising purposes and as a standard in alkalimetry; also for the separation of alkalies and magnesia, and for the detection and estimation of calcium. For use in analysis, therefore, the acid must conform to all the above tests. It has a distinct tendency to effloresce, even at 20°. The crystals must be obtained by interrupted crystallisation in order to avoid extraneous moisture. The dried crystals must show no signs of efflorescence, but on the other hand must be so well dried that no particles adhere to the sides when shaken up in a glass vessel; when these precautions are taken the acid remains unchanged, and the aqueous solution keeps well in dark bottles. A litre of the normal acid contains 63·03 gms.

Commercial Varieties.—The acid employed for technical purposes generally contains sulphuric acid and potash. The dehydrated acid has lately become a market article, and is used for some analytical purposes. It is not well adapted for standardising solutions, however, owing to its hygroscopic nature.

PALLADIUM AND ITS SALTS.—Palladium (Pd). At. wt., 106·7. The metal resembles platinum in appearance, lustre, and ductility. Palladium black is a grey spongy mass, soluble in hydrochloric acid in presence of air. The solid metal dissolves in aqua regia.

Tests for Impurities.—*Distinction between Palladium and Platinum Foil.*—A drop of alcoholic solution of iodine, when allowed to evaporate spontaneously on palladium foil, colours the metal black at the point of contact; this colour disappears on ignition. When platinum is similarly treated no colour appears.

Copper, Iron, etc.—To the solution in aqua regia ammonia in excess is added till the flesh-coloured precipitate of palladious ammonium chloride at first formed redissolves; hydrochloric acid gas, which precipitates the metal as the yellow palladious ammonium chloride, is then passed into the liquid, copper and iron remaining in solution. The chloride is

converted into spongy palladium on ignition. In the filtrate all remaining traces of palladium, as well as the copper, may be removed by means of zinc (Rössler). A still better method is to neutralise the solution in aqua regia with sodium carbonate, and precipitate the palladium and copper with mercuric cyanide. The precipitate is washed, ignited, dissolved in nitric acid, and on nearly neutralising this solution with sodium carbonate and boiling with potassium formate slightly acidified with acetic acid the palladium precipitates in large, thin, lustrous plates, while the copper remains in solution. The presence of copper may be seen from the greenish appearance of the mercury cyanide precipitate, which ought to be of a yellowish-white colour.

Quantitative Estimation.—Either the method given above may be used, or the metal may be precipitated as palladium iodide, and after washing converted into the metallic state by ignition. These methods are recorded in Fresenius, "Quant. Anal.," vol i., pp. 267, 365. Frenkel ("J.C.S.," 1893, A., ii., p. 195) has estimated the palladium in the alkaline palladious chlorides used for commercial purposes; by reduction with alcohol in alkaline solution he found 33·14 per cent. metal.

Uses.—Spongy palladium or palladium black is used in gas analysis for the separation of hydrogen when mixed with other gases, and also for the combustion of hydrogen or hydrocarbons with oxygen. On the use of palladium wire for the determination of hydrocarbons in the atmosphere see Coquillion, "Chem. Centralblatt," 1878, p. 104, and "J.C.S.," 1878, p. 773.

Palladium Asbestos.—Asbestos covered with the metal is used as a hydrogen absorbent, the method of preparation being given in Winkler's "Technical Gas Analysis," p. 77. It contains 50 per cent. palladium.

Commercial Varieties.—The commercial metal often contains a little iron and considerable quantities of copper. In addition to the pure metal in various forms, alloys with gold, silver, and copper are found in the market under the name of "Palladium en chaux". These are used in the manufacture of watches.

Palladium Salts.—The following are used in analysis:—

Palladium chloratum. Palladium protochloride ($PdCl_2$). This may be obtained by evaporating a solution of the metal in aqua regia to dryness, when it forms a dark brown hygroscopic mass. A 5 per cent. solution is also sold and is used as a reagent for several gases, such as illuminating gas and carbon monoxide, but particularly for iodine. The double salt of sodium and palladium is often used with advantage in place of the above, or a solution consisting of 1 part $PdCl_2$ + 2NaCl in 12 parts of water. It forms a dark red hygroscopic salt soluble in water and alcohol. The percentage of the metal in its salts can be easily estimated by titrating or precipitating in dilute solution with potassium iodide (see under "Palladium"). On the testing of the commercial alkaline palladious chloride, see under "Quantitative Estimation".

Palladium nitricum. Nitrate of palladium ($Pd(NO_3)_2$). This is formed by dissolving the metal in nitric acid containing a little nitrous acid, and is a brown hygroscopic salt (rhombic crystals), which always gives a turbid solution with water, owing to the presence of basic salts. The aqueous solution, especially when dilute, slowly deposits all its palladium in the basic form. It is used for the quantitative separation of chlorine and iodine, and is tested in the same way as the chloride. A characteristic of this salt, and of palladium and its salts generally, is the blackish-brown precipitate of the iodide which forms on adding potassium iodide.

PARANITROPHENOL, $C_6H_4 . OH(NO_2)[1 : 4]$.—Yellowish crystals soluble in alcohol and ether, sparingly soluble in water. M.p., 114°. Used as an indicator.

PERCHLORIC ACID.—Acid. perchloricum purum ($HClO_4$). Mol. wt., 100·47. Transparent colourless liquid. Sp. gr., 1·78.

Tests for Impurities.—*Residue.*—On heating 10 gms. of the acid in a porcelain basin no residue should remain behind, or only mere traces.

Hydrochloric Acid.—The solution (1 : 30) should show only a slight turbidity on adding silver nitrate.

Baryta.—As under "Chloric Acid," p. 79.

Sulphuric Acid.—The solution (1 : 30) must not show a

turbidity on adding hydrochloric acid and barium chloride, even after long standing.

Metals.—On diluting with water, and adding hydrogen sulphide, or ammonia and sulphuric acid, no turbidity must appear. The acid must show the theoretical amount of potassium perchlorate on precipitation in pure potassium chloride solution. The analysis is described in "Zeit. f. angew. Chem.," 1891, p. 692.

Quantitative Estimation.—The tests given above are sufficient, but a quantitative estimation may be made by precipitating as the potassium salt, according to Kreider (see "Potassium Perchlorate," p. 268).

Uses.—An aqueous solution of the acid precipitates potassium as perchlorate when the solution is not too dilute, and may therefore be used for the estimation and detection of potassium. Wense ("J.S.C.I.," 1892, p. 711) specially recommends its use for the former purpose, and prepares the acid as follows (loc. cit.): In a moderately thick glass retort 1 part of potassium perchlorate is distilled *in vacuo* with 2 parts of 90 per cent. sulphuric acid over a small naked flame. The distillate is then diluted and the sulphuric acid precipitated from the boiling solution with barium chloride. The acid is then evaporated on the water bath until it no longer smells of hydrochloric acid and has assumed a syrupy consistency when it is finally redistilled. For a simple method of preparing perchloric acid and its application for the determination of potassium, see also Kreider, "Chem. News," vol. lxxiii., 1896, p. 8.

PHENACETOLIN. — Formula $C_6H_4(OC_2H_5)(NHCOCH_3)$. White crystals. M.p., 134°-135°. Phenacetolin may be prepared by heating equal molecular proportions of phenol, concentrated sulphuric acid, and glacial acetic acid, and finally removing the free acid by means of water. The residue is used as an indicator, dissolving in caustic alkalies to a pale yellow, and forming intensely red compounds with the alkaline earths, pink with alkaline carbonates and deep pink with bicarbonates. On its sensitiveness, see "Table on Indicators," p. 142. For details regarding its use, see Cohn, "Indicators and Test Papers," p. 122.

PHENOL.—Phenol absolut. : carbolic acid (C_6H_5OH). Mol. wt., 94·08. Thin, colourless crystals, which lie loosely together, and have a distinct but not disagreeable odour. M.p., 43°. B.p., 180°.

Tests for Impurities.—*Volatility.*—The acid must volatilise completely.

Melting Point.—43°.

Solubility.—Soluble to a clear solution in 15 parts of water. When pure this is easily soluble in alcohol and ether.

Quantitative Estimation.—An ample guarantee of its purity is obtained if the sample conforms to the above tests.

Uses and Storage.—It is used for the detection of bromine, iron, etc., giving with the former a yellowish-white precipitate, and a violet colour in the presence of ferric chloride. It produces a blue colour with sulphuric acid when nitrous acid is present.

Millon's Reagent, which consists of a mercuric nitrate solution, containing nitrous acid, gives a yellow precipitate on boiling with carbolic acid, the precipitate dissolving in nitric acid to a rich red colour. On the preparation of Millon's Reagent, see p. 190.

Phenol Sulphonic Acid is used in the estimation of nitrogen by the Kjeldahl or Jodlbaur method, also for estimation of nitrates in water. It may be obtained by dissolving 50 gms. of absolute phenol in enough pure concentrated sulphuric acid of 66° Bé. to give 100 c.c. Carbolic acid must be carefully kept in bottles with a special mark, as it is a very active poison.

Commercial Varieties.—The acid is sold with a guaranteed melting point. Less pure varieties, with melting points from 34° to 35°, and the crude liquid carbolic acid are also found in the market.

PHENOLPHTHALEIN.—Phenolphthalein pur.

$$(C_6H_4 . OH)_2C(C_6H_4COO).$$

Mol. wt., 318·21. A yellowish-white, or almost white, crystalline powder, melting at 260°, very slightly soluble in water, easily in alcohol and ether.

Tests for Impurities.—*Volatility.*—0·5 gm. ignited in a platinum capsule must leave no residue.

Solubility in Alcohol.—A clear solution must be obtained with 10 parts of alcohol, and the alcoholic solution (1 : 100) must be colourless.

Sensitiveness.—The test is performed as under "Litmus Tincture," p. 177, and is as follows: On adding phenolphthalein to 250 c.c. of boiled and cooled distilled water, not more than 0·08 to 0·09 c.c. (3 drops) of $\frac{n}{10}$ alkali must be required to produce a violet colour untinged with red.

Note.—The above specification is given by Reinitzer ("Chem. News," vol. lxx., 1894, p. 240). R. T. Thomson ("J.S.C.I." 1887, p. 195; 1893, p. 432; "J.C.S.," 1883, A., p. 827; 1884, A., pp. 691, 869) employs a solution containing 0·5 gm. in a litre of 50 per cent. alcohol, of which 0·5 c.c. diluted with 100 c.c. of water, should use not more than 0·1 c.c. $\frac{n}{10}$ alkali to produce a red colour.

Uses.—The indicator may be used in the estimation of caustic alkali in presence of carbonate, and for the estimation of carbonate in presence of alkaline bicarbonate. In presence of the slightest excess of caustic alkali a distinct red colour is produced, which disappears on adding the merest trace of acid, even carbonic. Fixed alkali does not interfere with the reaction, but the indicator is useless in presence of ammonia or its salts. The purer the preparation the more delicate its action. The pure compound may be prepared, according to Baeyer, by heating together 5 parts of phthalic anhydride, 10 parts of phenol, and 4 parts of concentrated sulphuric acid for several hours at 115°-120°, the resulting compound forming a phthalein of phenol. The reaction does not take place quantitatively, many by-products being formed which interfere with the delicate properties of the indicator; these consist chiefly of resinous bodies giving coloured solutions in presence of acids. Details regarding this most useful and sensitive indicator are given in Sutton's "Vol. Anal.," p. 37.

A 1 per cent. solution in 50 per cent. alcohol may be advantageously used, and in titrating 100 c.c. of the solution the same quantity of the indicator should in all cases be added, 5 drops being a convenient quantity. On the use of phenolphthalein for detecting blood, see Merck's "Annual," 1910, p. 285.

Commercial Varieties.—These vary considerably in degree

of purity, often containing the above-mentioned resinous compounds.

PHENOL-SULPHONIC ACID.—Formula $C_6H_4(OH)(SO_3H)$. Mol. wt., 178·08. Fine crystalline powder.

Uses.—It is usually prepared in solution by mixing together 37 c.c. of concentrated sulphuric acid, 3 c.c. of distilled water, and 6 gms. of phenol. It is employed in the estimation of nitric acid and nitrates with which it gives a yellow colour on heating, intensified on adding excess of ammonia (picric acid). The colour is compared with that obtained with varying amounts of a standard solution of potassium nitrate until it is accurately matched.

PHENYL-HYDRAZINE.—Phenylhydrazin. puriss.

$$C_6H_5 . NH . NH_2.$$

Mol. wt., 108·11. Colourless, oily, faintly aromatic liquid, solidifying at a low temperature, and melting again at 18°. B.p., 230°. Easily soluble in alcohol and ether. The hydrochloride and acetate are used as a test for aldehydes, ketones and sugars (Allen's "Comm. Organ. Anal.," vol. i., pp. 218, 349). With sugars, hydrazones and osazones are formed, varying reactions being obtained according to the form of sugar present. The compound is also used for the detection of carbon disulphide, see "Benzene," p. 51. On its employment as a reagent, see Fischer, "J.S.C.I.," 1884, p. 331. On the estimation of the carbonyl oxygen in aldehydes and ketones, particularly acetone, by means of phenyl-hydrazine, see Strache, "J.S.C.I.," 1893, p. 185. Used at one time for estimating pentoses, and furfurol, now replaced by phloroglucin.

PHLOROGLUCIN.—Phloroglucin. puriss. $C_6H_3(OH)_3 2H_2O$. Mol. wt., 162·08. White or slightly yellow crystalline powder, parting with its water of crystallisation at 100°. On heating the substance rapidly it melts at from 200° to 209° (Bayer, "Ber. d. d. chem. Ges.," 19, p. 2186); 218° (Bernsthen). It dissolves rapidly in water, alcohol and ether.

Tests for Impurities and Quantitative Estimation.—The melting point, solubility in water, ether, and alcohol, and

presence of diresorcin, comprise the tests to be applied. In consequence of the presence of a small quantity of diresorcin the substance presents the well-known granular crystalline appearance, and according to Herzig and Zeisel ("J.C.S.," 1891, A., p. 125), this impurity is always to be found in the commercial preparations. The diresorcin may be detected as follows : A few milligrams of the phloroglucin are treated with 1 c.c. of concentrated sulphuric acid, 1 to 2 c.c. of acetic anhydride are then added, and the mixture heated for 5 to 10 minutes on the water bath at 100°; in presence of as little as 0·4 per cent. diresorcin a beautiful bluish-violet colour appears. A slight trace of this impurity need not be objected to, however, and it is therefore not essential that "phloroglucin puriss." should stand the above test. Nevertheless, there must not be any considerable quantity of diresorcin present, even in this preparation, and "phloroglucin pro analysi" which contains a few units per cent. of diresorcin should be rejected. This phloroglucin is tested by Skraup's method; see also C. Krauch, "Chem.-Ztg.," 1897, No. 2. Phloroglucin is used in the estimation of pentoses and pentosans for the precipitation of furfurol by Councler's method (Allen's "Comm. Organ. Anal.," vol. i., p. 546). Krüger and Tollens ("Zeit. f. angew. Chem.," 1896, p. 40), in estimating furfurol by the modification proposed by them, consider that Merck's phloroglucin pure for analysis, m.p., 210°, and containing a little diresorcin, may be used as advantageously as the compound freed from this impurity by Skraup's method. Merck now manufactures the latter preparation, but the price is much in excess of the former. It must show absolute freedom from diresorcin. It can also be used for the determination of furfurol, and for this purpose is preferred by Councler (see Krauch loc. cit.) to the "phloroglucin puriss., Merck," which formerly contained considerable quantities of diresorcin.

Uses.—Phloroglucin is employed as a test for lignin. On the detection of woody fibre in paper, see Allen's "Comm. Organ. Anal.," vol. i., p. 394; tissue containing lignin may be distinguished from cellulose by the intense red colour produced by phloroglucin and hydrochloric acid. The colour reactions of phloroglucin and carbon compounds in general are described

by Emil Nickel ("Zeit. f. anal. Chem.," 1889, p. 244 *et seq.*), and similar reactions with some of the essential oils by Ihl ("J.S.C.I.," 1889, p. 421).

Günzberg's phloroglucin and vanillin reagent, used for the detection of free hydrochloric acid in the gastric juice, is prepared by dissolving 2 gms. of phloroglucin and 1 gm. of vanillin in 30 gms. of alcohol ("Pharm. Ztg.," 1891, p. 393). A solution in nitric acid is used in microscopy as a decalcifying agent ("Rep. d. Chem.-Ztg.," 1891, p. 156).

Commercial Varieties.—The commercial compound often contains diresorcin, and has on that account a high melting point, as that substance melts at 310° (see also "Tests for Impurities").

PHOSPHO-MOLYBDIC ACID.—Acid. phospho-molybdaenic. cryst. ($12MoO_3$, PO_4H_3, $29H_2O$). Mol. wt., 2348·53. Yellow, lustrous crystals, easily soluble in water, and showing an acid reaction.

Tests for Impurities. — *Solubility, Heavy Metals, and Earths.*—2 gms. must dissolve completely in 10 c.c. of water, and the solution must give a heavy precipitate with a trace of ammonia, again becoming perfectly clear on adding excess. If to this solution ammonium sulphide and ammonium oxalate are added no change should be observed.

Quantitative Estimation.—The acid is dissolved in ammonia and the phosphoric acid estimated with magnesia mixture in the usual way. The molybdenum may also be estimated volumetrically by titration with permanganate (see Fresenius, "Quant. Anal.," vol. i., p. 290; see also under "Molybdic Acid," p. 182).

Uses.—The acid produces a yellow precipitate in strongly acid solutions of potassium, ammonium, rubidium, caesium, and thallium salts, the precipitates consisting of the respective phosphomolybdates; it also precipitates the alkaloids, and is one of the most important group reagents for their identification.

Commercial Varieties.—The crystals are often badly formed, and dissolve imperfectly. A solution of the acid is also sold as a reagent.

PHOSPHOTUNGSTIC ACID. — Acid. phospho-wolframic. cryst. $(P_2O_5 20WoO_3 11H_2O) + 16H_2O$. Mol. wt., 4292·38. Small, yellowish-green crystals. The following varieties are on the market : (1) the ordinary acid in crystals, (2) solution of the same, and (3) crystals absolutely free from NH_3 and N_2O_5. It has the special property of precipitating organic bases (see Allen's "Comm. Organ. Anal.," vol. iii., pt. ii., p. 136) but is also used for the precipitation of albumose and peptone ("Zeit. f. anal. Chem.," 1889, p. 195, and Allen's "Comm. Organ. Anal.," vol. iv., p. 84). It is also employed for estimating albumin in urine, for clearing the latter for polariscopic examination, also as a test for uric acid and phenols ("Merck's Annual," 1912, p. 355). Also suggested by A. Richaud and Bidau as a test for ferrous salts in urine, milk, etc. with which in presence of NaHO it gives a blue colour (Merck's "Annual," 1909, p. 139 ; 1910, p. 120). The commercial acid often contains a considerable quantity of ammonium nitrate.

PHOSPHORIC ACID. — Acid phosphoric puriss. (H_3PO_4). Mol. wt., 98·06. A clear, colourless, and odourless liquid. Sp. gr., 1·20. Containing 24 per cent. P_2O_5, or 33 per cent. H_3PO_4.

Tests for Impurities.—*Arsenic.*—3 gms. must give no reaction with Marsh's test, see "Sodium Carbonate," p. 296.

Nitric Acid.—On mixing 2 c.c. of the acid with 2 c.c. of sulphuric acid, and cautiously pouring 1 c.c. of ferrous sulphate solution on to the mixture, no colour must appear at the juncture of the two liquids.

Note.—According to Alex. Gunn, the acid sometimes contains quantities of nitric acid which remain undetected by the usual ferrous sulphate method, but infinitesmal traces may readily be detected by brucine, with formation of a red colour. Merck prepares an acid free from nitrogen for special analytical purposes, standing both the brucine and diphenylamine tests. For the latter test, see p. 98. The author applies the brucine test as follows : 2 gms. of brucine are placed in a test tube and moistened with 2 drops of water, after which 2 c.c. pure concentrated sulphuric acid are added ; the phosphoric acid is now carefully poured over the mixture ; after standing for a few minutes no red ring must have formed at the juncture of the two liquids.

Metals, Earths, etc.—No reaction must take place on adding hydrogen sulphide water. The acid, diluted with several times its volume of water, must show no turbidity or green colour on adding excess of ammonia, ammonium sulphide, and ammonium oxalate. On mixing with 4 parts by volume of alcohol the solution must remain clear.

Haloid Acids.—When diluted with 5 times its volume of water the acid must give no reaction with silver nitrate, either in hot or cold solution.

Organic Substances and Lower Oxides of Phosphorus.—5 c.c. of dilute sulphuric acid and 5 drops of potassium permanganate (1 : 1000) are added to 5 c.c. of the sample; on boiling the mixture for 5 minutes the red colour must still remain.

Note.—Salzer ("Pharm Ztg.," 1894, pp. 262, 211) found a sample which strongly reduced permanganate, and calls attention to the necessity of first of all proving the purity of the sulphuric acid used with reference to its action on permanganate.

Metaphosphoric Acid.—The dilute acid, when added drop by drop to a dilute solution of albumen, must produce no turbidity.

Sulphuric Acid.—When diluted with 10 times its volume of water, must give no reaction with barium chloride.

Ammonia.—On heating 2 c.c. with excess of caustic soda solution there must be no smell of ammonia, and the vapour evolved must not form white fumes on being approached with a glass rod dipped in dilute hydrochloric acid.

Note.—R. Huguet ("Chem. Centralblatt," 1894, p. 167) found a quantity of NaH_2PO_4, in a sample sold for medicinal purposes. In order to determine the amount present he precipitated with barium hydrate in the hot solution, and, after filtering, removed the excess of barium with sulphuric acid, and finally weighed the remaining sodium sulphate. The ammonium salt has also been found in the commercial acid. The presence of large quantities of salts may be detected by mixing the sample with alcohol, and an addition of two volumes of ether will render their presence more easily recognised

Quantitative Estimation.—The acid may be estimated by standard uranium solution, as described in Sutton's "Vol. Anal.," p. 284. On the volumetric estimation of the acid used for pharmaceutical purposes, see an article by C. Glücksmann,

"Pharm. Post.," 1895, No. 13. The qualitative tests and estimation of the specific gravity will generally be sufficient.

SPECIFIC GRAVITY OF PHOSPHORIC ACID SOLUTIONS AT 15°, AND PERCENTAGE OF H_3PO_4 AND P_2O_5.

Sp. Gr.	H_3PO_4 Per Cent.	P_2O_5 Per Cent.	Sp. Gr.	H_3PO_4 Per Cent.	P_2O_5 Per Cent.	Sp. Gr.	H_3PO_4 Per Cent.	P_2O_5 Per Cent.
1·0054	1	0·726	1·1262	21	15·246	1·2731	41	29·766
1·0109	2	1·452	1·1329	22	15·972	1·2812	42	30·492
1·0164	3	2·178	1·1397	23	16·698	1·2894	43	31·218
1·0220	4	2·904	1·1465	24	17·424	1·2976	44	31·944
1·0276	5	3·630	1·1534	25	18·150	1·3059	45	32·670
1·0333	6	4·356	1·1604	26	18·876	1·3143	46	33·496
1·0390	7	5·082	1·1674	27	19·602	1·3227	47	34·222
1·0449	8	5·808	1·1745	28	20·328	1·3313	48	34·948
1·0508	9	6·534	1·1817	29	21·054	1·3399	49	35·674
1·0567	10	7·260	1·1889	30	21·780	1·3486	50	36·400
1·0627	11	7·986	1·1962	31	22·506	1·3573	51	37·126
1·0688	12	8·712	1·2036	32	23·232	1·3661	52	37·852
1·0749	13	9·438	1·2111	33	24·058	1·3750	53	38·578
1·0811	14	10·164	1·2186	34	24·664	1·3840	54	39·304
1·0874	15	10·890	1·2262	35	25·410	1·3931	55	40·030
1·0937	16	11·616	1·2338	36	26·136	1·4022	56	40·756
1·1001	17	12·342	1·2415	37	26·862	1·4114	57	41·482
1·1065	18	13·068	1·2493	38	27·588	1·4207	58	42·208
1·1130	19	13·794	1·2572	39	28·314	1·4301	59	42·934
1·1196	20	14·520	1·2651	40	29·040	1·4395	60	43·660

Uses and Storage.—Phosphoric acid is used for the estimation of acetic acid in acetates by the distillation method. The acid ought to be stored in well-stoppered glass bottles.

Commercial Varieties.—The pure commercial acid is sold with a guaranteed specific gravity, those recorded in price lists ranging from 1·08 to 1·725. The commercial samples vary greatly as to purity (see notes under "Tests for Impurities").

PHOSPHORIC ACID (META). — Acid. phosphor. glaciale (PO_3H). Mol. wt., 80·05. Transparent, vitreous, hygroscopic lumps or sticks, easily soluble in water.

Tests for Impurities.—Tests as under "Phosphoric Acid". Sodium may be tested for after treatment with fuming hydrochloric acid; the pure acid ought to give a clear solution, but

if a sodium salt is present the latter remains undissolved in the form of chloride ("Zeit. f. anal. Chem.," 1888, p. 24). Commercial metaphosphoric acid generally contains the sodium salt, which is purposely added to preserve it.

Quantitative Estimation. — As under "Phosphoric Anhydride," the acid being first of all converted into orthophosphoric acid by dissolving in water which, after boiling the solution, is estimated either by the molybdate method or by titration with standard uranium solution.

Uses.—Metaphosphoric acid solution coagulates albumen, and is therefore used for its detection in urine. Blum uses for this purpose a solution of manganese metaphosphate, for the preparation of which see "J.S.C.I.," 1887, p. 387.

Commercial Varieties.—Prescott found from 23 to 38 per cent. sodium metaphosphate in several samples of glacial phosphoric acid. J. Hodgkin ("Chem. Trade Jour.," 1891, p. 142) gives analyses of various samples (see p. 228).

PHOSPHORIC ANHYDRIDE.—Acid. phosphoric. anhydric. (P_2O_5). Mol. wt., 142·08. Snow-white, odourless flakes, completely subliming on heating in a test tube, and emitting a hissing sound on dissolving in cold water.

Tests for Impurities.—The above characteristics show at once whether the sample is pure or otherwise; a yellowish colour indicates the presence of red phosphorus. Moisture causes the formation of metaphosphoric acid, and the sample thereby loses its volatility. Arsenious acid may be detected by treating the aqueous solution with hydrogen sulphide.

Quantitative Estimation.—The anhydride is dissolved in water, boiled to convert it into phosphoric acid, and the latter estimated by the molybdic acid method.

Uses and Storage.—In organic synthesis it presents a most useful dehydrating agent, and it may also be advantageously used in the drying of gases ("Zeit. f. Anal. Chem.," 1887, p. 628; 1888, p. 1 *et seq.*). According to Shenstone and Beck ("J.C.S.," 1893, T., p. 475) commercial P_2O_5 sometimes contains the lower oxides; these prove detrimental to its properties as a drying agent. These observers sublime the commercial preparation in a current of oxygen for certain purposes

(see loc. cit.). Bottles containing the substance must have perfectly fitting stoppers.

Commercial Varieties. — These often fail to show the characteristic fine white appearance or contain moisture, and in some cases unconverted phosphorus (see also under "Uses").

Analyses of Glacial Phosphoric Acid.

Sample.	Origin.	Form.	Free HPO_3.	Combined HPO_3.	Equal to $-PO_3$.	Total HPO_3.	Total by Uranium.
A.	Made by ammonia process . .	Lumps	48·00	43·52	42·98	91·52	91·84
B.	English . .	,,	52·80	40·00	39·50	92·80	93·14
C.	,, . .	,,	46·08	39·36	38·87	85·44	85·40
D.	German . .	,,	31·68	52·80	52·14	84·48	84·98
E.	,, . .	Sticks	36·48	47·36	46·77	83·84	83·70
F.	European, obtained from America .	Lumps	42·21	37·89	37·41	80·10	80·41
G.	Experimental	,,	44·16	46·72	46·14	90·88	90·65
H.	,, from microcosmic salt .	,,	None	—	—	—	78·12

Analyses of Glacial Phosphoric Acid—*continued.*

Total Base.	Ammonium.	Sodium.	Equal to HPO_4, $12H_2O$.	Water.	Silica.	Arsenic.
8·05	8·05	None	—	Traces	0·54	Traces
7·82	6·48	1·34	10·44	—	—	0·08
9·79	0·07	9·72	75·63	5·60	—	Traces
14·09	0·05	14·04	109·30	2·40	—	—
13·49	0·06	13·43	104·48	3·25	—	—
10·20	None	10·20	79·30	10·10	—	—
10·10	4·87	5·23	40·67	Traces	—	—
22·50	—	22·50	—	—	—	—

PICRIC ACID — TRINITROPHENOL. — Acid. picronitric. puriss. cryst. ($C_6H_2(NO_2)_3OH$). Mol. wt., 228·57. Thin, pale yellow plates of a brilliant lustre, easily soluble in alcohol, ether and benzol, soluble in hot, but less soluble in cold, water (1 : 86). Melting point, 122°.

Tests for Impurities.—The following substances must be looked for particularly (see also Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 148):—

(1) *Resinous Matter.*—One part of picric acid is dissolved in 60 parts of hot water, sulphuric acid to the extent of 1-2000 part of the picric acid present is added, and the solution filtered; resin, if present, remains on the filter.

(2) *Oxalic Acid.*—This is sometimes present in small quantities, and originates in the manufacture. It may be detected by the microscope, since the colourless prisms can be easily distinguished from the yellow rhombic plates of picric acid. It may also be estimated by precipitation with lime water, or with ammonia and calcium chloride.

(3) *Saltpetre, Glauber's Salt,* and *Common Salt* may all be estimated in the residue by well-known methods after extracting the acid with hot alcohol until the washings are colourless.

(4) *Sugar.*—This may be determined after exactly neutralising with potassium carbonate, carefully evaporating the filtrate from the potassium picrate to dryness on the water bath, and repeatedly extracting the residue with strong alcohol. The alcoholic filtrate is evaporated to dryness, when the residue may be tested for sugar by Trommer's method. For the detection of mono- and dinitrophenol, Allen ("Jour. Soc. Dyers and Col.," 4, p. 84, and Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 149) recommend the following: Two stoppered bottles are taken, and an equal measure of an approximately 1 per cent. solution of bromine added to each; to one of the bottles is added the same measure of a 1 per cent. picric acid solution; potassium iodide in excess is now added to both, and the iodine liberated estimated with $\frac{n}{10}$ thiosulphate solution. The difference in the amount of bromine absorbed represents the amount of above impurities present.

Uses and Storage.—The acid is used for the precipitation

of alkaloids, presenting a ready method for their detection, also for precipitating albumin, and for the estimation of naphthalene (W. P. Jorissen and J. Rutten, "J.S.C.I.," 1909, p. 1179). It is poisonous, and when suddenly heated is liable to explode. Great care should be exercised in storing it.

Commercial Varieties.—Samples containing inorganic impurities are often found.

PICROCARMINE.—This substance is employed as a stain in microscopical investigations, and a solution of picrocarminate of ammonia, prepared by Ranvier's method, may be advantageously used for such purposes. L. Gedölst considers the sodium salt much to be preferred to that of ammonia, and gives a method for its preparation ("J.S.C.I.," 1887, p. 543). For the preparation of the ammonia compound, see p. 73.

PICROLONIC ACID. — l-para-Nitrophenyl-3-Methyl-4-isonitro-5-Pyrazolone,

$$NO_2 . C_6H_4 . N\begin{matrix}\diagup COC \equiv N : O(OH) \\ \diagdown N \equiv C - CH_3.\end{matrix}$$

Yellow powder, insoluble in water, soluble in alcohol. Used in the detection of alkaloids. M.p., about 125°.

PLATINUM.—Platina (Pt). Mol. wt., 195·2. The solid metal has a silvery-white appearance, with a slight grey tint.

Platinum black, or platinum in a fine state of division, has the colour its name implies. The spongy form may be obtained by ignition of ammonium-platino-chloride, and is of a pale grey colour. The metal dissolves in aqua regia.

Tests for Impurities and Quantitative Estimation.—The metal is dissolved in aqua regia and the solution evaporated on the water bath. The chloride thus formed is converted into spongy platinum by strong ignition in a porcelain crucible. On extracting the mass with dilute nitric acid, only traces of the residue ought to be dissolved out (see "Platinum Chloride"). The ammonium-platino-chloride formed, when ammonium chloride is used as the precipitant, can also be converted into the metallic state by ignition. Iridium, when present, remains undissolved when the solution in aqua regia is diluted with 4 or 5 times its volume of water. Accord-

ing to Mylius and Förster ("J.S.C.I.," 1892, p. 690) small quantities of impurities may be detected by the following method: Three separate samples are taken; the first is tested for palladium, iridium, and ruthenium by the lead method of Deville and Stas; a second sample is dissolved in aqua regia, reduced by addition of formic acid, and the iron estimated in the filtrate; while the third is volatilised by means of carbon monoxide and chlorine, and the residue tested for rhodium, silver, copper, and lead. If 10 gms. of the metal are taken for each test, it is possible to estimate the following quantities: Iridium, 0·003; ruthenium, 0·005; rhodium, 0·004; palladium, 0·01; iron, 0·001; copper, 0·002; silver, 0·002; and lead, 0·002 per cent. A description of the method may be found in the article cited. An excellent test for the quality of platinum vessels consists in adding in succession the purest and most concentrated hydrochloric, sulphuric and nitric acids, and heating each acid to boiling, care being taken to thoroughly cleanse the vessel each time; on evaporating the acids to dryness no residue must remain behind.

Uses.—A variety of vessels is manufactured from the metal, and in the form of platinum black it finds use as an oxidising agent in organic chemistry, and in ultimate organic analysis may be used in place of copper oxide. In the preparation of platinum bichloride for the estimation of potash (see Merck's "Annual Report," 1892, p. 75) and for other analytical purposes only the purest platinum containing a maximum of 0·01 per cent. total impurities, should be used.

Commercial Varieties.—Nearly all commercial platinum contains iridium, which, however, does not interfere with its conversion into manufactured articles generally. It nearly always contains distinct traces of copper, iron, rhodium, palladium, and ruthenium. Mylius and Förster (loc. cit.) found the commercially pure metal to contain 99·26 per cent. platinum, 0·32 iridium, 0·13 rhodium, no palladium, 0·04 ruthenium, 0·06 iron, and 0·07 copper. Several years ago W. C. Heraeus ("J.S.C.I.," 1891, p. 773) and Mylius and Förster (loc. cit.) found an easy method of preparing a very pure metal in large quantities, containing only 0·01 per cent. of impurities, chiefly iridium; this quality has since been placed on the market.

An alloy of the metal with iridium is often used for the manufacture of platinum vessels and wire, and is also better adapted for making the sulphuric acid concentrating plant than the pure metal. As gold is even less affected by the action of concentrated sulphuric acid, the apparatus is often gilded.

PLATINUM BICHLORIDE.—Platina chlorata. Platinic chloride sicc., pur. ($PtCl_4$ + 2HCl, $6H_2O$). Mol. wt., 518·07.[1] Dry, reddish-yellow crystalline mass, deliquescent, giving a dark but pure yellow solution with water.

Tests for Impurities.—*Solubility.*—1 gm. dissolved in 10 c.c. of absolute alcohol must give a clear solution; the aqueous solution must behave likewise. When the solution shows a red or dark brown colour the presence of protochloride or iridium may be inferred.

Note.—The author has frequently found commercial samples which left a considerable greenish-yellow residue on solution in alcohol, and evidently contained protochloride. These samples generally show a dark brownish colour in aqueous solution (1 : 10), and ought to be rejected. As mentioned before, the colour may also be due to iridium. For the preparation of good platinum chloride solution, free from protochloride, see, for example, "Zeit. f. angew. Chem.," 1896, p. 544.

Residue on Ignition.—2 gms. are thoroughly ignited, and the residue of spongy platinum digested with dilute nitric acid (5 c.c. of acid, sp. gr. 1·2, and 20 c.c. of water) on the water bath for a quarter of an hour; after filtering, the solution is evaporated and ignited; only a maximum of from 4 to 5 mgms. of residue ought to remain.

Note.—According to Hager ("Handbuch der pharm. Praxis"), traces of residue cannot be avoided, as they are derived from the vessels in which the platinum has been dissolved.

Sulphuric Acid.—The solution must give no reaction with barium chloride, even after long standing.

[1] The true platinum chloride ($PtCl_4$) may be obtained by precipitating a solution of the above with silver nitrate, filtering and evaporating the filtrate. For analytical purposes, particularly potash estimation, the bichloride is used; it contains about 37·6 per cent. metal. A preparation is also sold containing about 40 per cent., and obtained by further evaporation of the solution. It may be used for analyses, if pure.

Note.—Hollemann ("Analyst," xvii., p. 80) detected this impurity in a commercial sample, but the author cannot corroborate the statement.

Baryta.—A solution (1 : 20) must show no turbidity, even after long standing, after adding a few drops of sulphuric acid.

Quantitative Estimation.—The platinum is precipitated with pure potassium chloride as the platinochloride, filtered through a filter paper which has been dried at 130°, and, after careful but not long-continued washing with alcohol-ether the precipitate is dried for about 20 minutes at 130° and weighed. The method is described by Precht ("J.C.S.," 1880, A., p. 577; see also Ruer, "J.C.S.," 1897, A., ii., p. 160). A pure platinum bichloride ought to give a theoretical yield of the double salt with pure potassium chloride (see Precht, loc. cit.). When a metal containing iridium is used for the preparation of the chloride the iridium is also dissolved, but, according to Precht (loc. cit., p. 512), traces of this impurity do not interfere with the potash estimation. Larger quantities may be detected by the quantitative tests given, and by the solution showing a brown colour.

Uses and Storage.—The salt is used for the detection and estimation of potash and ammonia, and in solution as a group reagent for alkaloids. For analytical purposes the chloride must be prepared from the purest platinum. Owing to its hygroscopic nature it must be kept in well-stoppered bottles or in sealed glass tubes.

Commercial Varieties.—See above.

POIRIER'S BLUE.—The calcium or sodium salt of triphenylrosanilinenitrisulphonate. Light blue powder soluble in water and in alcohol.

Uses.—Is employed as an indicator in acidimetry especially for the estimation of acids combined with weak bases, e.g. the alkaloids, aniline, etc. A 0·2 per cent. solution in water is employed. With acids it gives a blue colour and with alkalies red (Merck's "Index," p. 292).

POTASSIUM ACETATE.—Kalium aceticum, puriss. (CH_3CO_2K). Mol. wt., 98·13. White, hygroscopic, crystalline

powder, easily soluble in water (1 : 0·437) and alcohol but insoluble in ether.

Tests for Impurities.—*Alkalinity and Solubility.*—The aqueous solution must be clear, and though it should give no reaction with phenolphthalein, it renders red litmus paper blue.

Earths, Metals, Sulphates, and Chlorides.—The aqueous solution (1 : 20) must give no reaction with sodium carbonate, ammonium oxalate, barium chloride, or hydrogen sulphide, and the latter must neither precipitate nor colour the solution. There ought to be only a slight turbidity with silver nitrate, after acidifying with nitric acid.

The flame test must show only a violet colour.

Quantitative Estimation.—See under "Sodium Acetate," p. 287.

Uses and Storage.—The salt is used for the detection of tartaric acid, and must be carefully stored.

POTASSIUM BICARBONATE.—Kalium bicarbonicum, puriss. cryst.: bicarbonate of potash ($KHCO_3$). Mol. wt., 100·11. The crystals (monoclinic) remain unchanged in contact with the air, and dissolve in 4 times their weight of water.

Tests for Impurities and Quantitative Estimation.—See under "Potassium Carbonate" and "Potassium Hydrate," puriss., pp. 241 and 253 respectively.

Uses.—On account of the readiness with which it crystallises the salt may be obtained very pure, and is frequently used in place of carbonate. Mohr employs it instead of the carbonate in the preparation of $\frac{n}{10}$ potassium arsenite (see "Arsenious Acid," p. 43). On the employment of potassium bicarbonate for making standard solutions, see "J.C.S.," 1897, A., ii., p. 593.

Commercial Varieties.—These generally contain chlorides and sulphates.

POTASSIUM BICHROMATE.—Kalium bichromicum, puriss.: acid chromate of potash ($K_2Cr_2O_7$). Mol. wt., 294·2. Large red triclinic prisms, dissolving to a clear solution in water (1 : 11).

Tests for Impurities.—The chromium is determined by the method mentioned below (see "Uses").

Sulphuric Acid.—3 gms. are dissolved in 100 c.c. of water; on addition of hydrochloric acid and barium chloride, no change must take place after 12 hours' standing.

Note.—It is necessary to add sufficient acid in the above test, otherwise barium chromate may be precipitated.

In using bichromate for the oxidation of organic compounds, previous to the estimation of their sulphuric acid, it is essential to obtain the salt free from SO_3.

Sulphuric acid is sometimes tested for as follows: The salt is completely reduced with hydrochloric acid and alcohol, barium chloride is then added and the solution allowed to stand for 12 hours. Fresenius employs this method in testing the mixture of potassium and sodium chromates, and sodium carbonate, used for sulphur estimations in ultimate analysis. Mohr also reduces the chromic acid to avoid the formation of barium chromate, which is difficultly soluble in dilute acids ("Lehrbuch der Titrirmethode," 6th ed., p. 265).

According to Post ("Chem.-techn. Analyse"), an accurate quantitative determination may be conducted as follows: The salt is dissolved in water, the sulphate and chromate precipitated with barium chloride, and the solution heated with hydrochloric acid and alcohol. The barium chromate is reduced, the chromic acid being converted into chromium chloride, and the remaining barium sulphate is boiled several times with hydrochloric acid, and well washed. Post considers it inadmissible to reduce the chromic acid before precipitating with barium chloride, otherwise part of the sulphuric acid might escape precipitation through formation of ethyl sulphuric acid.

Another method is to dissolve the bichromate in water and add barium chloride; the precipitate must dissolve completely in pure hydrochloric acid.

Chloride.—The dilute hot solution, after acidifying with nitric acid, must give no reaction with silver nitrate.

Solubility and Alkaline Earths.—2 gms. must dissolve in 30 c.c. of water to an absolutely clear solution, and this solution must show no turbidity on addition of ammonia and ammonium oxalate, even after long standing.

Quantitative Estimation.—See under "Uses" and "Sodium Bichromate".

Uses.—Potassium bichromate is used in ultimate analysis for the estimation of hydrogen, nitrogen, and sulphur; for the

latter purpose the salt must contain no sulphuric acid. It is often used as a laboratory reagent, particularly as an oxidising agent, similarly to chromic acid. The detection of chlorides is sometimes effected by means of bichromate and concentrated sulphuric acid, for which purpose the salt must not contain that impurity. It is also employed in the preparation of standard solutions for the estimation of iron, chromium, uranium, etc., for liberating a known quantity of iodine from potassium iodide, and is used for the estimation of lead, bismuth, etc., by Baumann's gasometric method, and lastly, as an oxidation test for strychnine. Meineke prepares a pure sample by exactly neutralising a known quantity of chromic acid (free from H_2SO_4) with the purest potassium hydrate, adding again the same quantity of chromic acid, recrystallising 6 times, and finally fusing in a bath of potassium bichromate (Liebig's "Annalen," 1891, p. 357). He determined the purity of this preparation by Zulkowski's method, based on the decomposition of potassium iodide by chromic acid. For the result of Meineke's analyses, see loc. cit. For the preparation of standard solutions a salt must be used which shows a percentage of chromium in accordance with that of the salt investigated by Meineke. The correct composition of such a salt is found by estimating the chromium by Zulkowski's method (see Liebig's "Annalen," 1891, loc. cit.).

Commercial Varieties.—The ordinary commercial kinds often contain considerable quantities of sulphuric acid. These contain 98 to 99 per cent. of the salt, and are sold with a guaranteed percentage of about 68 per cent. CrO_3.

POTASSIUM BINIODATE. — Kalium biiodicum, puriss. ($KIO_3 + HIO_3$). Mol. wt., 389·95. White crystals, giving a clear solution with 18·66 parts of water at 17°.

Tests for Impurities.—The salt must contain 100 per cent., and must give a clear solution with water.

Quantitative Estimation.—According to C. Meineke (Liebig's "Annalen," 1891, p. 363), the acid iodate of potash may be used in place of iodine for even the most accurate estimations. The salt should have the composition KHI_2O_6, as stated above, and to ascertain if this is the case, the acidity is estimated with

$\frac{n}{10}$ potash, using phenolphthalein as indicator, and the percentage of iodic anhydride is calculated from the iodine liberated from potassium iodide by means of hydrochloric acid, according to the equation,

$$KHI_2O_6 + 10KI + 11HCl = 11KCl + 6H_2O + 12I.$$

For examples of this method, see Meineke, loc. cit.

As a blank test Meineke estimates the amount of iodine liberated from potassium iodide with the iodate alone, which must be exactly 1-12th part of the total iodine set free when hydrochloric acid is used, as in above equation. The potash is determined in the iodate by decomposing with hydrochloric acid and weighing the potassium chloride thus obtained.

Commercial Varieties.—Meineke states that the market article is very pure, particularly that sold by Messrs. E. Merck, which he has found to give from 100·001 to 100·010 per cent. on analysis.

POTASSIUM BISULPHATE. — Kalium bisulphuricum, puriss.: acid sulphate of potash ($KHSO_4$). Mol. wt., 136·17. Colourless rhombic crystals, giving a clear solution with water.

Tests for Impurities.—*Heavy Metals, etc.*—The solution (1 : 20) must be clear and must give no reaction with hydrogen sulphide, or ammonia and ammonium sulphide.

Chlorides.—The solution (1 : 30) must show no turbidity with silver nitrate.

Arsenic.—Test in Marsh's apparatus as under "Sodium Carbonate," using 2 gms. of the sample.

Nitric Acid.—The solution (1 : 20) must show no reaction on applying the indigo test.

Quantitative Estimation.—The sulphuric acid is estimated gravimetrically with barium chloride in aqueous solution, or volumetrically with normal alkali. 1 c.c. normal alkali = 0·13617 gm. $KHSO_4$.

When the potassium has to be estimated, barium chloride is carefully added to the aqueous solution until only traces of sulphuric acid are left, the filtrate is then evaporated and the potassium estimated with platinum bichloride in the usual way.

Uses and Storage.—It is used as a flux in the analysis of minerals, and must be carefully stored.

Commercial Varieties.—The raw commercial bisulphate is obtained as a by-product from several industries.

POTASSIUM BITARTRATE.—Cremor tartari, pur.: cream of tartar ($KHC_4H_4O_6$). Mol. wt., 188·16. White, odourless, crystalline powder (rhombic) soluble in 20 parts of boiling, and 200 parts of cold water. Insoluble in alcohol and ether.

Tests for Impurities.—*Sulphates and Chlorides.*—The aqueous solution (1 : 20) must give no reaction with barium chloride after adding dilute nitric acid and filtering, and only a slight turbidity with silver nitrate.

Metals.—The solution, after addition of dilute ammonia, must show neither colour nor precipitate with hydrogen sulphide.

Lime.—1 gm. of the tartrate with 5 c.c. of dilute acetic acid are allowed to stand for half an hour, and repeatedly shaken during that time; the solution is then mixed with 25 c.c. of water, allowed to settle, and the clear liquid poured off; on adding to this a little oxalate of ammonium solution no change must appear within 1 minute's time.

Ammonia.—No smell of ammonia must be given off on heating with caustic soda.

Quantitative Estimation.—Simple methods are given in Sutton's "Vol. Anal.," 7th ed., p. 112; see also below.

Uses and Storage.—Pure cream of tartar, complying with the demands of the German Pharmacopœia, is used for the preparation of the chemically pure salt (see later). It must be kept in well stoppered bottles.

Commercial Varieties.—Other varieties, known as Venetian and French tartar exist, both containing more or less calcium tartrate. Argol is a crude tartar obtained from wine lees.

For the analysis of commercial cream of tartar, see Allen, "J.C.S.," 1896, A., ii., p. 584.

POTASSIUM BITARTRATE (AS A STANDARD FOR NORMAL SOLUTIONS), ($KHC_4H_4O_6$). Mol. wt., 188·16.

Bornträger recommends the use of this salt for standardising both alkaline and acid solutions. It is prepared from white

cream of tartar by heating the salt for several hours with 1 part of water and 0·1 part hydrochloric acid (sp. gr., 1·13); the solution is then stirred till cold, the precipitate filtered, well washed, recrystallised from pure water, and dried at 100°.

It may be regarded as pure if it requires as much acid after careful ignition as it required alkali before, both quantities agreeing with the theoretical. For this test Bornträger uses a normal hydrochloric acid which has been standardised on transparent Iceland spar, and standardises his normal alkali on this solution. In employing the chemically pure tartrate to standardise all normal acids a weighed quantity is thoroughly charred over a low flame, the platinum capsule and contents placed in a covered beaker, extracted with water, and normal acid gradually added until, after boiling, there is a slight but distinct acid reaction. The solution is then titrated back with normal alkali till there is no reaction with neutral litmus paper; 3·7632 gms. of potassium bitartrate, or the quantity of potassium carbonate obtained from it, should exactly neutralise 20 c.c. normal alkali or acid respectively.

POTASSIUM BROMATE. — Kalium bromicum, puriss.: bromate of potash ($KBrO_3$). Mol. wt., 167·02. Colourless hexagonal crystals, difficultly soluble in water.

Tests for Impurities.—The quantitative estimation determines the purity of the salt; it must contain 100 per cent.

Quantitative Estimation.—The sample is dried, and 0·1 gm. dissolved in water with a few gms. of potassium iodide and about 15 c.c. hydrochloric acid; the iodine liberated is titrated with $\frac{n}{10}$ sodium thiosulphate. 1 c.c. $\frac{n}{10}$ thiosulphate = 0·0027833 gm. potassium bromate.

Uses.—The salt is used for the quantitative estimation of carbolic acid. According to Feit and Kubierschky ("Chem.-Ztg.," 1891, p. 351, and "J.S.C.I.," 1891, p. 486) bromic acid is a particularly energetic oxidising agent, and can therefore be used to great advantage in the quantitative estimation of hydrogen sulphide, sulphurous acid, oxalic acid, etc.; for these determinations potassium bromate is employed (for details, see loc. cit.).

Commercial Varieties.—Samples containing large quantities of potassium bromide have often been met with.

POTASSIUM BROMIDE. — Kalium bromatum, puriss.: bromide of potassium (KBr). Mol. wt., 119·02. Bright, colourless cubic crystals, unaffected by the atmosphere. Easily soluble in water (1 : 1·7), solution in which must be neutral.

Tests for Impurities.—*Potassium Bromate and Potassium Carbonate.*—On spreading the ground sample on a white porcelain plate, and adding a few drops of dilute sulphuric acid no yellow colour must immediately appear, and on touching the sample with moist red litmus paper a violet-blue colour must not appear at once.

Note.—With the above reaction it is possible to detect 0·02 per cent. of potassium bromate. The equations are as follow :—

$$2KBrO_3 + H_2SO_4 = K_2SO_4 + 2HBrO_3$$
$$5HBr + BrO_3H = 3H_2O + 3Br_2.$$

In testing for the smallest traces of bromate the salt is dissolved in water and a small crystal of potassium iodide added, along with a few drops of starch solution and dilute sulphuric acid; the appearance of a blue colour denotes the presence of bromate.

Sulphate of Potash, Metals, and Barium.—The aqueous solution (1 : 20) must show no reaction with hydrogen sulphide, barium nitrate, or dilute sulphuric acid.

Iodides.—5 c.c. of the solution (1 : 20) are mixed with a few drops of ferric chloride solution and a little chloroform; the latter must not be coloured violet.

Note.—On the test for iodides, see also "Hydrobromic Acid, puriss.".

Chlorides.—See "Quantitative Estimation," also "Hydrobromic Acid".

Sodium.—The salt, when heated on platinum wire, must give a violet colour throughout the flame.

Quantitative Estimation.—The estimation is carried out volumetrically with $\frac{n}{10}$ silver nitrate (16·99 gms. per litre), particularly for the purpose of determining the potassium chloride which exists in nearly every commercial sample. The German Pharmacopœia (iii.) gives the following method: 10 c.c. of an aqueous solution (3 gms. in 100 c.c.) of the potassium bromide, previously dried at 100°, must not use more than 25·4 c.c. of $\frac{n}{10}$ silver nitrate, using potassium chromate as indicator. The more chloride there is present the more silver

nitrate will be used, and perfectly pure potassium bromide, tested under the above conditions, should use 25·21 c.c. $\frac{n}{10}$ silver nitrate, but with 1 per cent. potassium chloride present, 25·35 c.c., and with 6 per cent. KCl, 25·79 c.c. are used. With sodium bromide and ammonium bromide under certain conditions the above test is useless (Vulpius, "Arch. d. Pharm.," 1887, p. 404, and "J.S.C.I.," 1887, p. 567).

In the case of inorganic salts, bromine is liberated by distillation with sulphuric acid and manganese dioxide, the bromine being passed into excess of a solution of ammonia which has been exactly neutralised with nitric acid; the ammonium bromide solution thus obtained is titrated with $\frac{n}{10}$ silver nitrate.

Uses.—Solutions of bromide and bromate of potassium are employed for the quantitative estimation of carbolic acid ("Pharm. Germ., ii.").

Commercial Varieties.—These often contain several per cent. of potassium chloride. An instance of commercial bromide containing chlorate is cited ("Arch. d. Pharm.," 1888, p. 388), and sometimes samples are found in a very moist condition. H. Helbing and W. Passmore ("J.S.C.I.," 1892, p. 705) obtain the following results on comparison of six samples of English and American bromide:—

	English.		*American.*			
	1.	2.	3.	4.	5.	6.
Moisture	0·95	1·22	0·56	0·36	0·35	1·29
Chlorides as KCl . .	0·13	0·13	4·96	5·91	4·52	5·92

According to these figures the American bromide is of rather poor quality.

POTASSIUM CARBONATE.—Kalium carbonic. puriss.: carbonate of potash (K_2CO_3). Mol. wt., 138·20. A white granular powder, giving a clear solution with its own weight of water, and containing at least 99·5 per cent. K_2CO_3.

Tests for Impurities.—The tests for alumina, other metals, silicic, sulphuric, nitric, and phosphoric acids, and chlorine, are conducted as under "Potassium Hydrate," p. 253.

Potassium Cyanide is detected by adding a little ferrous sulphate and ferric chloride to the solution; on the subsequent

addition of hydrochloric acid in excess no blue colour must appear.

Potassium Sulphide, etc.—1 part by volume of the solution (1 : 20) when poured into 20 volumes $\frac{n}{10}$ silver nitrate must give a yellowish-white precipitate which does not darken on applying gentle heat ("Pharm. Germ., iii."). Regarding this silver nitrate test, see Bolling, "Arch. d. Pharm.," 1888, p. 541.

When dilute hydrochloric acid is added to the dry salt in a test tube, and a piece of filter paper saturated with lead acetate held over the mouth of the tube, no brown colour must appear on the paper. The detection and estimation of caustic alkali in alkaline carbonates may be effected by Dobbin's method ("J.S.C.I.," 1888, p. 829); see further under "Potassium Hydrate, puriss., Quantitative Estimation," p. 255.

Sodium.—The salt when heated on platinum wire must give a pure violet flame without yellow tinge.

Quantitative Estimation.—The volumetric estimation of the K_2CO_3 present is generally sufficient, and the method, using standard hydrochloric acid, is exhaustively described in works on volumetric analysis (see also under "Sodium Carbonate, Quantitative Estimation"). 1 c.c. normal acid = 0·06910 gm. K_2CO_3. The percentage of potassium is estimated as follows: The carbonate is dissolved in water, acidified with hydrochloric acid (sulphuric acid, if present, being removed by barium chloride, excess of which must be avoided), and the potash estimated with platinic chloride. When examining inferior qualities of potassium carbonate this estimation is important, as a simple titration would give too high results. The author found apparently 96 per cent. K_2CO_3 on titrating an 80 per cent. sample, as the sample contained soda. The accurate determination of sodium and potassium is described under "Potassium Hydrate," p. 255. Sulphates and chlorides are determined in the sample after acidifying with hydrochloric and nitric acids respectively, and precipitating with barium chloride and silver nitrate. The quantitative estimation of nitric acid is performed by the reduction method with zinc, iron, and caustic potash (see note on "Test for Nitric Acid," under "Potassium Hydrate, puriss.").

On the analysis of carbonate of potash, see Crookes' "Select Methods of Chemical Analysis," p. 18 *et seq.*

Uses.—Potassium carbonate is used chiefly in analysis as a solvent for insoluble sulphates and silicates, and for this purpose a mixture of the pure carbonates of potash and soda is used, the salts being of course free from sulphuric and silicic acids. The carbonate is also used for the preparation of normal solution of potassium arsenite, and the salt in this case must be absolutely free from sulphur compounds. Mohr uses potassium bicarbonate for this on account of the facility of obtaining it in a very pure state.

Commercial Varieties.—Samples of varying degrees of purity (from 50 to 98 per cent. K_2CO_3) can be obtained, the crude potassium carbonate often containing only 50 per cent., and, in addition to moisture, large quantities of chloride, sulphate, sodium carbonate, and other salts, such as cyanide and sulphide; it is generally of a red or bluish colour from the presence of iron and manganese salts. The author has found 82 per cent. K_2CO_3 and 12 per cent. Na_2CO_3 in an 84 per cent. sample. Better samples (about 90 per cent.) contained about 2 per cent. Na_2CO_3. The better class of purified commercial carbonates contain from 90 to 98 per cent. K_2CO_3, and only a few per cent. sulphates, chlorides, etc. Potassium carbonate,

Description of the Potash.	Quality.	$K_2CO_3 + KOH$ Calculated as K_2CO_3.	Na_2CO_3.	K_2SO_4.	KCl.	Observer.
American carbonate .	1	104·4	1·4	4·0	2·0	F. Mayer
,, ,,	2	71·2	8·2	16·1	3·6	Author
,, pearlash .	—	71·3	2·3	14·3	3·6	Payen
Tuscany carbonate .	—	74·1	3·0	13·4	0·9	Author
Illyrian ,, .	—	89·3	—	1·2	9·5	H. Grüneberg
Russian ,, .	—	69·6	3·0	14·1	2·0	Payen
Transylvanian ,, .	—	81·2	6·8	6·4	0·6	H. Grüneberg
Hungarian ,, (for domestic purposes)	—	44·6	18·1	30·0	7·3	Author
Galician carbonate .	—	46·9	3·6	29·9	11·1	Author
Refined sheep's fleece	—	72·5	4·1	5·9	6·3	Author
French beetroot .	1	90·3	2·5	2·8	3·4	Author
,, ,, .	2	80·1	12·6	2·5	3·4	Dénimal
German potash . .	1	92·2	2·4	1·4	2·9	H. Grüneberg
,, ,, . .	2	84·9	8·2	2·8	3·5	Author

puriss., is free from sulphates and silicates, and contains only infinitesimal traces of chlorides and bicarbonate. This latter impurity may occur in larger quantity, so that the carbonate appears to be mixed in parts with large transparent crystals of bicarbonate.

The table given on p. 243, by A. W. Hofmann, taken from Schmidt's "Pharm. Chemie," shows the percentages found in various samples of commercial carbonate.

POTASSIUM CHLORATE.—Kalium chloricum, puriss.: chlorate of potash ($KClO_3$). Mol. wt., 122·56. Colourless, monoclinic shining crystals, dissolving in water (1 : 17) to a clear, neutral solution.

Tests for Impurities.—*Earths and Chlorides.*—The solution in water (1 : 20) must be neutral and must remain unchanged after addition of either ammonium oxalate or silver nitrate.

Metals (*Lead*).—3 gms. are dissolved in 30 c.c. of warm water; the solution must be clear, and must not be coloured on adding hydrogen sulphide.

Nitrates.—On heating 1 gm. of the salt with 5 c.c. caustic soda solution and 0·5 gm. zinc filings and iron powder, no smell of ammonia must be given off.

Note.—On other tests for nitrates, see "Pharm. Ztg.," 1888, p. 20.

Arsenic.—Test as given under "Chloric Acid," p. 79. For this test 20 gms. of the sample are used.

Sulphates.—The solution (1 : 20) must not show the sulphuric acid reaction with barium chloride, even after long standing.

Sodium.—See under "Potassium Carbonate," p. 242.

Quantitative Estimation.—An excess of hydrochloric acid is added to the chlorate, and the whole distilled; the chlorine passing over is retained in a solution of potassium iodide, and liberates an equivalent quantity of iodine, which is titrated with $\frac{n}{10}$ thiosulphate; 1 c.c. thiosulphate solution = 0·0020427 gm. potassium chlorate. As an example, if 0·1 gm. of the chlorate were taken, this would require 48·9 c.c. $\frac{n}{10}$ thiosulphate if the compound were chemically pure (see also under "Chloric

Acid"; Topf, "Zeit. f. anal. Chem.," 1887, p. 295, and Sutton's "Vol. Anal.," 7th ed., p. 166).

Thorpe and Herbert ("J.C.S.," 1876, p. 856) describe a method for the quantitative estimation of chloric acid in chlorates by the copper-zinc couple.

Uses and Storage.—As chlorate of potash is a powerful oxidising agent, it is useful in many chemical investigations, in forensic chemical analysis for the destruction of the organic substance, in ultimate organic analysis for the estimation of carbon, and for the analysis of sulphur compounds. It decomposes on triturating with easily oxidisable matter, and many accidents have occurred through handling it incautiously. An instance is quoted in the "Pharm. Ztg.," 1892, p. 161, where a pharmaceutical chemist had both hands blown off, his eyes totally destroyed, and eventually died of his injuries, through grinding chlorate and sulphur together. The handling and storing of this product must be conducted with the greatest care.

Commercial Varieties.—The salt is now generally sold in a very pure condition, but the following impurities are recorded in literature on the subject. Hilger states that he once found lead in a commercial sample, a fact which has to be taken into account in using the chlorate for forensic work. R. Otto calls special attention to the necessity of testing the salt for arsenic before using it for the purpose just mentioned. This author also found lead (R. Otto, "Ausmittelung der Gifte," 1884). A commercial sample, which, on heating on the water bath, evolved chlorine and contained tartaric acid, is mentioned ("Pharm. Ztg.," 1889, p. 246). Inferior qualities of the chlorate contain chloride, and Böckmann remarks that hypochlorites are sometimes present; their presence explains the smell of chlorine sometimes emitted from gas holders containing oxygen.

POTASSIUM CHLORIDE.—Kalium chlorat. puriss. : chloride of potassium (KCl). Mol. wt., 74·56. Colourless cubic crystals, giving a clear, neutral solution with water (1 : 3).

Tests for Impurities.—*Solubility, Sulphuric Acid, Earths, Metals, etc.*—These tests are conducted as under "Sodium Chloride".

Sodium.—See under "Potassium Carbonate," p. 242.

Quantitative Estimation.—The chlorine is determined by titration with $\frac{n}{10}$ silver nitrate in aqueous solution, and the potassium as potassio-bichloride of platinum. On the accurate analysis of the potassium chloride used for technical purposes, see works on technical chemical analysis (*inter alia*, Böckmann, "Chem.-techn. Untersuchungs-methoden," 3rd ed., p. 525, or J. König, "Untersuchung landwirthsch. und gewerbl. wichtiger Stoffe," Berlin, 1891, p. 193).

Uses.—Among other uses it is employed in the estimation of hydrofluosilicic acid.

Commercial Varieties.—The salt is also sold for technical and agricultural purposes, with guaranteed percentages of the pure salt, such as 70, 80, 90, and 99 per cent. KCl.

The potash factories guarantee the presence of not more than $\frac{1}{2}$ per cent. sodium chloride with certain kinds. Potassium chloride generally contains slight traces of the chlorides of rubidium and caesium ("Chem.-Ztg.," 1892, p. 335), and manganese and calcium chlorides are also found in varieties for technical purposes.

POTASSIUM CHROMATE.—Kalium chromicum, flav. puriss. : neutral chromate of potash (K_2CrO_4). Mol. wt., 194·20. Yellow rhombic pyramid crystals, dissolving in water to a clear solution, and showing only a faint alkaline reaction (1 : 1·7).

Note.—A solution of the pure salt shows a slightly alkaline reaction with litmus and turmeric. According to De Vrij ("Arch. d. Pharm.," 1887, p. 753) neutral potassium chromate really shows a neutral reaction towards phenolphthalein.

Tests for Impurities.—The salt must not contain any small red crystals of the bichromate.

Solubility.—See above.

Free Alkali.—On dissolving 0·1 gm. in 25 c.c. of water and adding a few drops of phenolphthalein no red colour must appear.

Sulphuric Acid and Chlorides.—Tests as under "Potassium Bichromate," p. 235.

Alumina and Alkaline Earths.—The solution (1 : 20) must give no reaction with ammonia or oxalate of ammonium.

Quantitative Estimation. — See under "Potassium Bichromate," p. 235.

Uses.—The salt is employed as an indicator in the titration of chlorides with silver nitrate solutions, and, further, in the preparation of several standard solutions, e.g., in the estimation of baryta. It is also used in the estimation of quinine (De Vrij, "J.C.S.," 1887, A., p. 404; 1889, A., p. 1091).

Commercial Varieties.—Some qualities are found containing strong traces of sulphates, and others giving strongly alkaline and cloudy solutions.

POTASSIUM CYANIDE.—Kalium cyanat. puriss.: cyanide of potassium (KCN). Mol. wt., 65·12. A white powder, or in fused lumps, easily soluble in water, and containing about 99 per cent. KCN.

Tests for Impurities.—*Potassium Sulphide.*—The solution should give a pure white precipitate with lead acetate.

Silicic Acid.—See under "Potassium Hydrate, puriss.," p. 254. This test must be conducted where there is no chance of inhaling the fumes, as *hydrocyanic acid* is given off on evaporating with hydrochloric acid.

Carbonic Acid, Chlorides, etc.—See note below.

Sodium.—See "Commercial Varieties".

Note.—Pauly applies the following tests to potassium cyanide, which are recorded in the "Real-Encyklopädie der Gesammten Pharmacie". The pure cyanide must dissolve completely in hot alcohol with a little water added; an insoluble residue, effervescing with acids, shows presence of potassium carbonate; if, on treating the alcoholic solution with hydrochloric acid, carbonic acid is given off, the presence of cyanate may be inferred. The aqueous solution, containing hydrochloric acid in excess, must neither give a blue precipitate with ferric chloride (potassium ferrocyanide), nor a red precipitate (thiocyanate) with the same reagent. Barium chloride must not produce a white turbidity (sulphate). In testing for chloride a quantity is ignited with two parts of potassium nitrate and ten parts potassium carbonate, and after the cyanogen has been destroyed the mixture is dissolved in water acidified with nitric acid and silver nitrate added; no precipitate must appear.

Quantitative Estimation.—The quality of the cyanide is best ascertained by Liebig's well-known method with standard silver nitrate. 5 gms. of the sample are dissolved in 500 c.c.

of water; 25 c.c. of this solution are diluted, a few drops of dilute caustic potash added, and, after addition of a little sodium chloride, $\frac{n}{10}$ silver nitrate is run in until, on stirring, a permanent turbidity appears (see also Sutton's "Vol. Anal.," 7th ed., p. 190). As a solution of the cyanide in water soon decomposes, the titration must be done at once. 1 c.c. $\frac{n}{10}$ silver nitrate = 0·013014 gm. KCN.

Uses and Storage.—In the dry state the cyanide acts as a strong reducing agent, and analytically finds especial use in the reduction of tin oxide, antimonic acid, and arsenic sulphide. It is also of important service in blowpipe analysis, and is used quantitatively for various separations, as for example, nickel and zinc (Wöhler), and nickel and cobalt. In volumetric analysis it is used for the estimation of copper, and other determinations. Owing to its extremely poisonous nature great care must be exercised in storing it. In contact with air it gives off hydrocyanic acid.

Commercial Varieties.—Cyanide for technical purposes of very varying degrees of purity is found in the trade, but some are sold with a guaranteed percentage and containing cyanate (the quality manufactured by Liebig's method); other kinds contain also sodium cyanide (Wagner's Method). R. Kayser ("Chem.-Ztg.," 1898, p. 1148, and "J.S.C.I.," 1893, p. 518) calls attention to the fact that the cyanide manufactured at the present time often consists of mixtures of the sodium and potassium salts, a fact which must be taken into account when testing, as otherwise a sample might be passed as 100 per cent. which contained a considerable quantity of sodium cyanide, in many cases amounting to 15 per cent. A sample tested by Stillman ("J.S.C.I." 1893, p. 41) apparently contained 105·87 per cent. KCN, and consisted of 17 per cent. NaCN and 83 per cent. KCN. Commercial cyanide of potash containing about 40 per cent. of cyanogen is generally used in gold extracting (see Leroy, "Chem.-Ztg.," 1897, p. 122).

POTASSIUM FERRICYANIDE.—Ferri-kalium cyanatum, puriss.: red prussiate of potash ($K_6Fe_2Cy_{12}$). Mol. wt., 657·92. Large red monoclinic crystals, giving a clear solution with water (1 : 2·5).

Tests for Impurities.—*Solubility.*—See above.

Sulphuric Acid and Ferrous Salts.—The solution (1 : 30) must not show a blue coloration with ferric chloride, and must be free from sulphuric acid (see "Potassium Ferrocyanide," p. 251).

Chlorides and Sodium.—Tests as under "Potassium Ferrocyanide". A quantitative estimation must also be performed, and must show from 99·6 to 100 per cent.

Quantitative Estimation.—W. Gintl (Mohr, "Titrirmethode," 6th ed., p. 237) reduces the salt with sodium amalgam, and estimates the ferrocyanide as given under that salt (see p. 252). Fe × 11·782 = potassium ferricyanide.

It is better to estimate the oxygen in the salt by a gas volumetric method (Quincke, "Zeit. f. anal. Chem.," 1892, pp. 1 and 436; Baumann, "Zeit. f. angew. Chem.," 1892, p. 113; "J.C.S.," 1892, pp. 526, 527, 538), which consists in decomposing an alkaline solution of the salt with hydrogen peroxide, according to the equation—

$$K_6Fe_2Cy_{12} + 2KOH + H_2O_2 = 2K_4FeCy_6 + 2H_2O + O_2.$$

The oxygen is then measured. 1 c.c. at 760 mm. pressure and 0° C. = 0·029447 gm. potassium ferricyanide. Baumann (loc. cit.) recommends to transfer the ferricyanide dissolved in a little water to the outer space of the generating flask of an azotometer, and then to add about 5 c.c. caustic potash solution (1 : 2). The hydrogen peroxide is then placed in the inner tube of the flask; if up to 50 c.c. of gas are anticipated, 5 c.c. of 2 per cent. H_2O_2 are used; if from 50 c.c. to 100 c.c., then 10 c.c. are added. The flask is then immersed in the cooling vessel, the stopper inserted, and when the temperature has become constant, the test is proceeded with in the ordinary way. Reliable results can only be obtained if both flask and graduated tube are immersed in water of the same temperature during the whole time of the experiment. When the liquids in the flask have been well mixed and shaken and the gas measured (at the same temperature throughout) the volume must be reduced to 0° and 760 mm. The volume found multipled by 29·447 gives the weight of potassium ferricyanide, as 657·724 parts by weight of ferricyanide evolve 31·92 parts by weight of oxygen. 1·42908 mgms. of oxygen (i.e., 1 c.c. at 0° and 760 mm.) are

equal to 29·447 mgms. potassium ferricyanide. On decomposing dry recrystallised potassium ferricyanide by this method Baumann obtained the following results: 1·0015 gms. of the salt were taken, pressure at 0°, 709 mm.; temp., 17°; volume of gas liberated, 39·5 c.c.; when reduced, 33·99 c.c. = 1·0008 gms. ferricyanide (99·93 per cent.). Such experiments conducted in Lunge's nitrometer, or an azotometer, may be recommended to those who often require to analyse potassium ferricyanide and similar compounds easily tested by gas volumetric methods. In addition to the above-mentioned papers by Quincke and Baumann, may be mentioned a former paper by Baumann, a criticism of his work by Lunge and Marchlewski, and his reply, all of which are published in "Zeit. f. angew. Chem.," 1891 (see also "J.C.S.," 1892, A., p. 538). As Gintl's titration method does not give accurate results, the above process is to be recommended. Some manufacturers analyse the salt by determining the nitrogen by Kjeldahl's method, or by estimating the impurities. The results by Kjeldahl's method are said to be very accurate, and to agree with the refraction method (estimation of the impurities). It is therefore advisable for those not accustomed to gas volumetric analysis to use the latter methods as a check.

Uses and Storage.—Red prussiate of potash is chiefly used as a test for ferrous oxide. Plugge ("Arch. d. Pharm.," 1887, p. 343, and "J.S.C.I.," 1887, p. 840) uses the salt for the separation of alkaloids. Quincke employs it in the gas volumetric estimation of hydrogen peroxide, alkalies, alkaline earths, etc. According to Luckow and others both the ferri- and ferrocyanide are well adapted for the volumetric estimation and separation of the metals ("J.C.S.," 1892, A., pp. 1129, 1527). The ferricyanide, and also the standard solutions of ferri- and ferrocyanide, must be kept in brown bottles, as they are much affected by light. Luckow even uses brown glass burettes when titrating. Potassium ferricyanide is also sensitive to atmospheric influence, and must therefore be evaporated when recrystallising at from 50° to 60°. For several volumetric methods it is necessary to use a ferricyanide which is perfectly free from such impurities as the sodium salt, sulphates, chlorides, and ferrous salts.

A ferricyanide test paper is also prepared, see p. 144. A method for preparing a specially delicate paper is given in "Pharm. Ztg.," 1895, p. 767.

Commercial Varieties.—These often fail to give a perfectly clear solution in water, and contain, as does also the ferrocyanide, traces of sulphates. Commercial samples must be tested for chlorides (see "Potassium Ferrocyanide,") as the red prussiate is prepared from the yellow by passing chlorine gas into a solution of the latter. The author has sometimes found very pure samples containing about 99 per cent. among the best commercial ferricyanides.

POTASSIUM FERROCYANIDE.—Ferro-kalium cyanatum, puriss.: yellow prussiate of potash ($K_4FeCy_6, 3H_2O$). Mol. wt., 422·4. Large lemon-yellow quadratic crystals, easily soluble in water (1 : 3) to a clear solution.

Tests for Impurities.—*Solubility.*—See above.

Sulphuric Acid.—The solution (1 : 20) must show no change, even after long standing, on addition of a little hydrochloric acid and barium chloride.

Note.—According to a communication received from a ferrocyanide factory the sulphuric acid is more accurately determined quantitatively as follows: The sample is finely ground, and 5 gms. of a good average sample are dissolved in water and poured into a solution containing 7 to 8 gms. ferric chloride (free from H_2SO_4), and the solution acidified with hydrochloric acid and filtered; a measured portion of the filtrate is precipitated with barium chloride and treated in the usual manner, with this exception, that the precipitate is first washed with water, then with caustic soda solution, again with water, then with very dilute hydrochloric acid, and finally with water, this being done to remove traces of ferrocyanide compounds.

Chlorides.—Potassium chloride, when present, may be detected by decomposing 0·5 gm. of the salt with 1 gm. of pure nitre in a porcelain crucible, extracting with water and acidifying with nitric acid; on adding silver nitrate no turbidity must appear. According to C. Luckow ("Chem.-Ztg.," 1892, p. 164, and "J.C.S.," 1892, A., pp. 1129, 1527), the presence of chlorine can be detected with silver nitrate after precipitation of the ferrocyanide with the nitrate of a metal.

Sodium is detected as follows: To the solution of 1 gm. of the ferrocyanide, acidified with a little hydrochloric acid, ferric chloride is added in excess. A part of the filtrate is taken, and the excess of ferric salt removed by ammonia; the filtrate is then tested for sodium by the well-known method with potassium metantimoniate. A quantitative estimation may also be made, and must show 99·6 to 100 per cent.

Quantitative Estimation.—The estimation is based on the reaction which takes place on adding potassium permanganate to a dilute solution of the salt, acidified with hydrochloric acid. De Haen and Fresenius (Fresenius, "Quant. Anal.," vol. i., p. 378) first standardise the permanganate on a solution of chemically pure ferrocyanide, containing 10 gms. of the salt per litre. Of this solution 10 c.c. are placed in a porcelain basin, diluted with 250 c.c. of water containing some hydrochloric acid, and the permanganate added until the characteristic red colour appears; if the sample uses 50 c.c. permanganate solution, this is equal to 0·1 gm. potassium ferrocyanide, or 1 c.c. = 0·002 gm. To find the percentage of a commercial sample 10 gms. are dissolved in water, made up to 1 litre, and titrated as above. The permanganate may also be standardised on ferrous iron, according to Mohr; in this case Fe × 7·564 = potassium ferrocyanide. On the commercial analysis of the yellow prussiate, see Böckmann, "Chem.-techn. Untersuchungen," 3rd ed., vol. i., p. 510 *et seq.* Another reliable method is as follows: A weighed quantity of the salt is evaporated with dilute sulphuric acid in a platinum capsule, the excess of acid removed by heating, and the residue carefully ignited; acid is again added, the solution reduced with zinc and a few drops of copper sulphate solution, and titrated with permanganate. The moisture can be determined at the same time by drying the powdered salt at 110° till constant in weight, and subtracting the theoretical percentage of water of crystallisation from the total loss.

Uses and Storage.—The salt is used chiefly as a reagent for the precipitation of copper, iron, and other metals; also for the estimation of strychnine ("J.C.S.," 1890, A., p. 1318; 1897, A., p. 852). It must be kept in brown glass bottles. For the preparation of a seminormal solution of potassium

ferrocyanide for volumetric determination of zinc., see "Zeit. f. angew. Chem.," 1896, pp. 464, 567.

Commercial Varieties.—Large crystals of ferrocyanide of potassium sometimes contain a considerable amount of sulphuric acid; Otto found as much as 14 per cent. H_2SO_4 in a sample having a good appearance superficially. L. Blum ("J.C.S.," 1891, A., p. 1293) states that commercial samples often contain a large quantity of sodium. The author has often found the better commercial salts to be very pure (about 99 per cent.), containing only a few tenths of a per cent. sulphates and chlorides. On standing in contact with the air the crystals usually become blue on the edges owing to the formation of Prussian blue.

POTASSIUM HYDRATE.—Kalium hydricum: caustic potash (KOH). Mol. wt., 56·11. The three following varieties are used in analytical laboratories:—

(1) The purest preparation—namely, "Potassium Hydrate, puriss.," also called "Potassium hydrate, prepared from potassium sulphate and barium hydrate".

(2) Potassium hydrate, pure, also designated as "pure by alcohol".

(3) Ordinary pure potassium hydrate.

To avoid error and confusion, the writer has recorded in detail the tests to be applied to each separate preparation; the three qualities also vary in price.

1. **Potassium Hydrate Puriss.**—White, crystalline lumps.

Tests for Impurities.—*Solubility, Alumina.*—5 gms. when dissolved in 10 c.c. of water must give a clear, colourless solution. On adding excess of acetic acid to this solution, rendering alkaline with slight excess of ammonia, diluting to 100 c.c., heating in a beaker for half an hour on the water bath (the smell of ammonia being then only faint; 1 or 2 drops more being added if the smell is entirely gone), and allowing the solution to stand for several hours at the ordinary temperature, no precipitate, flocculent or otherwise, must appear.

Calcium, Heavy Metals.—The slightly alkaline solution from the above test must show no reaction with ammonium oxalate or ammonium sulphide.

Silicic Acid.—On evaporating 5 gms. in dilute hydrochloric acid to dryness, and drying the residue for half an hour at 100°, a clear solution must result on dissolving this residue in 250 c.c. of water, containing a little hydrochloric acid.

Sulphuric Acid.—3 gms. are dissolved in about 50 c.c. of water, slight excess of hydrochloric acid added, the solution heated and barium chloride added; no reaction must take place after several hours' standing.

Chlorides.—After acidifying the solution (1 : 20) with nitric acid only a slight opalescence must be observable on addition of silver nitrate.

Nitric Acid.—(*a*) 2 gms. are dissolved in 10 c.c. of water, and the solution acidified with dilute sulphuric acid; on adding one drop of ordinary indigo solution (see p. 148) previously diluted with double its volume of water, and about 10 c.c. of strong sulphuric acid, the blue colour must not be discharged, even after standing for some time.

(*b*) 50 gms. of the hydrate are dissolved in 200 c.c. of water; then 5 gms. of a mixture of arsenic-free zinc powder and iron (reduced by hydrogen) are added; the mixture is transferred to a flask of 500 c.c. capacity, provided with a receiver containing about 10 c.c. dilute sulphuric acid (1 : 100); the apparatus is allowed to stand for a few hours, a small flame is then applied and the distillation so regulated that about 15 c.c. distil over in three-quarters of an hour. The distillate is now made alkaline with a little of the purest caustic potash, and 2 c.c. of Nessler's reagent added; only a slight and distinctly yellow opalescence must appear, and not a heavy, brownish-red precipitate forming a thick layer and causing the solution to appear turbid.

Note.—The author first gives a method representing a guarantee of the salt's freedom from nitric acid (the indigo method), and adds, as a check, a simple and accurate test in the form of the well-known reduction method with zinc and iron. This test when performed as described above is so accurate that 1 mgm., or even less, can be detected in 25 gms. of caustic potash or soda. In proof of this the author prepared various samples of 50 gms. each of pure potash and soda, to which he added 2 mgms. of nitric acid, and applied the test, the reliability of which was at once proved by the appearance of heavy brownish-red precipitates, turning the liquids turbid and quite

opaque. Allowance must be made for a slight yellowish colour or opalescence, as this change is often observed where no alkali is present, but when water alone is boiled with zinc and iron. It is therefore advisable to perform a blank test in any event, as Nessler's reagent is very delicate. The author uses iron and zinc powders which have been reduced by hydrogen, and specially prepared for the purpose, as he has often found commercial zinc dust to give a brown colour with Nessler's reagent, on shaking with water.

Caustic alkalies containing several per cent. of nitrates and nitrites are often sold. In making a quantitative estimation the reduction method is used, alcohol being substituted for water in the distillation; standard sulphuric acid is placed in the receiver, and after distillation the acid is titrated with standard barium hydrate. The author used this method in making a large number of quantitative nitric acid estimations at the Agricultural Testing Station of Münster (see J. König and C. Krauch, "Landwirtsch, Jahrbücher," 1882, p. 159, and J. König, "Chem. d. Nahrungsmittel," vol. ii., 1883, p. 669).

Carbonic Acid, Potassium, and Other Salts.—The sample must give a clear, colourless solution on heating with 90 per cent. alcohol (5 gms. potash and 25 gms. alcohol, sp. gr. 0·83), and on filtering and washing the filter with the above solution there must not remain behind a residue of more than 0·02 gm. The test for CO_2 described under "Potassium Hydrate, pure by Alcohol," may be used as a check on the above method.

Phosphoric Acid.—5 gms. are dissolved in 50 c.c. of water, a large excess of nitric acid, and nitric acid solution of ammonium molybdate are added; after 2 hours' standing at a gentle heat no precipitate must appear.

Sodium and Sodium Sulphide.—See "Potassium Carbonate," p. 242, also with reference to "Sodium," see below.

Quantitative Estimation.—The caustic alkalies are titrated with normal acid, using litmus as indicator. 1 c.c. equals 0·05611 gm. KOH. Where there is a mixture of caustic alkali and carbonate present, as is often the case with many sodium and potassium carbonates, and less pure caustic potash, these must be determined separately by first ascertaining the total alkalinity and then estimating the caustic alkali by precipitating the carbonate with barium chloride solution (forming barium carbonate and potassium chloride), and, after filtration, titrating the hydrate with normal acid. The percentage of

carbonate is found by difference. The method is described in detail in works on volumetric analysis (see Sutton, "Vol. Anal.," 7th ed., p. 56); direct estimation of alkaline hydrate in presence of carbonate, using phenolphthalein as indicator, is also described in the same work (see also Lunge "J.S.C.I.," 1897, p. 262). In estimating the percentage of sodium hydrate in potassium hydrate, a weighed quantity of the sample is acidified with hydrochloric acid and then dried; the mixed chlorides are weighed, dissolved in a little water, and the potassium estimated with platinum bichloride in the usual way. On subtracting the weight of KCl thus found from the weight of the total chlorides, the difference gives the amount of NaCl present. Both Na and K are then calculated to the hydrates. This method gives accurate results (see also "Potassium Carbonate," p. 242). If the sodium is in large amount a simple method is to convert to sulphates by treating with sulphuric acid, and ignite, the proportion of K and Na can then be calculated from the weight of the mixed sulphates.

Uses, Storage, and Normal Solution.—Caustic potash is extensively used in chemical analysis as a precipitating and separating agent, as, for example, in the precipitation of copper oxide and the separation of iron and alumina; also as a solvent for minerals, and in the preparation of standard caustic solutions. It is also used in the determination of nitric acid by the reduction method (see p. 254), and for the estimation of sulphur in organic and inorganic substances. In conjunction with charcoal both the alkaline hydrates are effective solvents for ores and insoluble silicates ("Zeit. f. Anal. Chem.," 1891, p. 226).

It is often used in organic synthesis, in ultimate organic analysis, and gas analysis for the absorption of carbon dioxide. The three qualities of caustic potash find use in analysis according to the purpose for which they are required, and all must be kept in well-stoppered bottles.

Normal Caustic Potash Solution.—This solution must contain 56·11 gms. KOH per litre, and is similarly prepared to normal caustic soda (*q.v.*). It is standardised on either normal hydrochloric or sulphuric acid, or on potassium tetroxalate (*q.v.*).

Note.—Normal Alkali Solutions.—One litre of a normal alkali solution must contain the hydrogen equivalent in grams of a mono-acid base, or in the case of a bivalent substance one-half the molecular weight, and must exactly neutralise one molecule of monobasic acid or one-half molecule of a dibasic acid. Using the latest atomic weights the following gives the number of grams per litre :—

	Per Litre.
Potassium hydrate	56·11 gms.
Sodium hydrate	40·01 „
Ammonium hydrate	35·05 „
Hydrochloric acid	36·5 „
Nitric acid	63·02 „
Sulphuric acid	49·04 „
Acetic acid ($C_2H_4O_2$)	60·05 „
Oxalic acid, anhydrous ($C_2H_2O_4$) . .	45·01 „
Oxalic acid, crystallised ($C_2H_2O_4$, $2H_2O$)	63·03 „
Tartaric acid ($C_4H_6O_6$) . . .	75·03 „
Phosphoric acid (H_3PO_4) . . .	32·69 „
Citric acid, anhydrous ($C_6H_8O_7$) . .	64·02 „
Citric acid, crystallised ($C_6H_8O_7$, H_2O)	70·03 „

These last three acids are tribasic, one-third of the molecule being taken; the normal acid solutions are standardised on the same principle as the normal alkaline.

Commercial Varieties.—Gerlach ("Chem. Industrie," 1886, p. 245) found 74·4 per cent. KOH in pure commercial crystallised potassium hydrate having the composition, $KOH + H_2O$. It is well known that perfectly anhydrous potassium hydroxide (KOH) cannot be prepared; the fused potassium hydrate (free from water), and even caustic potash, containing more than 10 per cent. of water, have considerable action on the silver vessels in which it is necessary to prepare them, and become of a greyish appearance owing to the presence of this metal. Pure potassium hydrate for analytical purposes is, on this account, always prepared containing 20 per cent. of water. It is incorrectly stated in some books that anhydrous potassium hydroxide (KOH) has a perfectly white appearance; W. Dittmar ("Chem.-Ztg.," 1891, p. 1581) also remarks on the inaccuracy of this statement. Regarding the impurities of

commercial preparations, the author has found large quantities of alumina, sulphuric acid, nitric acid, and baryta present in samples marked "Pure potassium hydrate, prepared from potassium sulphate and barium hydrate". It is, of course, impossible to use such impure preparations for analytical purposes, particularly in the separation of iron and alumina, and it is most important, when purchasing the best and more expensive potash, to be on guard against such impure qualities. Messinger ("J.C.S.," 1889, A., p. 313) states that commercial potassium hydrate nearly always contains nitrites. This observer employs a normal alkali solution (56 gms. per litre) in his acetone method, and tests this solution as follows: To 20 c.c. of the potash solution are added 0·1 to 0·2 gm. potassium iodide, and after acidifying with hydrochloric acid the iodine liberated is titrated with $\frac{n}{10}$ thiosulphate and starch solution. On the presence of boracic acid, see "Sodium Hydrate".

2. Potassium Hydrate, pure by Alcohol (KOH + aq.).—White crystalline lumps, or short sticks.

Tests for Impurities.—*Solubility, Alumina, Lime, etc.*—10 gms. must give a clear, colourless solution with 40 c.c. of water. The solution is diluted to about 100 c.c., acidified with acetic acid, and slight excess of ammonia added; only a slight turbidity should appear after 5 minutes' standing, but no flocculent precipitate; on further adding ammonium oxalate and ammonium sulphide, the solution must not become turbid. It is only after long standing that a slight precipitation of alumina takes place.

Nitric and Sulphuric Acids.—See "Potassium Hydrate, puriss.," p. 254.

Chlorides.—Test as under "puriss.". The solution (1 : 20) must also show only a faint opalescence with silver nitrate.

Silicic Acid.—On evaporating 5 gms. in dilute hydrochloric acid to dryness, and drying the residue at 100°, only a slight turbidity should result on dissolving in 150 c.c. of water.

Carbonic Acid.—2 gms. are dissolved in 10 c.c. of water; on pouring this solution into a mixture of 8 c.c. hydrochloric acid (1 : 12) with 8 c.c. of water no effervescence must occur.

Uses and Quantitative Estimation.—See "Potassium Hydrate, puriss.," p. 255.

Commercial Varieties.—The commercial potash of this class varies very considerably in purity, and has often a grey colour. It contains alumina (which may be expected in lower grade samples), chlorides, and particularly nitrates.

3. Ordinary Pure Caustic Potash (KOH + aq.).—Short, white, crystalline sticks or lumps. The solution in water must be clear and colourless.

Tests for Impurities.—*Nitric Acid.*—2 gms. are dissolved in 10 c.c. of water, acidified with sulphuric acid, and 1 drop of indigo solution in twice its volume of water added ("Solutio Indici," p. 148); on now adding 10 c.c. concentrated sulphuric acid the colour must not be discharged within a few minutes.

Carbonic Acid.—See above, under "Potassium Hydrate, pure by Alcohol".

Uses and Quantitative Estimation.—See "Potassium Hydrate, puriss.".

Commercial Varieties.—This quality, contrary to the other pure hydrates, contains about 1 per cent. of chlorides; also silica and alumina. On dissolving 5 gms. in 100 c.c. of water, acidifying with hydrochloric acid and adding excess of ammonia, a flocculent precipitate of alumina appears at once (see "Test for Alumina," in "Potassium Hydrate, pure by Alcohol"). The percentage of hydrate varies from 75 to 85 per cent.

Dunstan ("Pharm. Jour.," 3rd series, vol. xvi., p. 778; see also "J.C.S.," 1886, T., p. 646, on the formation of hyponitrites) found 0·34, 0·47, 0·56, 0·74, and 1 per cent. nitrous acid in an ordinary fused caustic potash employed as a reagent; it also contained nitrates and about 4·5 per cent. chlorides, etc. Such preparations must be rejected. Owing to the use of saltpetre to obtain a pure white preparation samples are found containing even large quantities of nitrates, and chlorates may also be detected. Good ordinary caustic potash contains but little soda (about 0·5 per cent. Na_2CO_3); two commercial samples showed 0·47 and 1·9 per cent. K_2SO_4.

Ordinary potash is sold on percentage of alkalinity. The following may be given as examples of analyses from a chemical factory:—

(1) About 100 per cent. alkalinity . 77-80 per cent. KOH.
(2) ,, 115-120 ,, ,, . 86-88 ,, KOH.

AVERAGE ANALYSES.

	(1) Alkalinity about 100 per Cent.	(2) Alkalinity about 115-120 per Cent.
	Per Cent.	Per Cent.
Potassium hydrate	78·12	86·67
Potassium carbonate	3·70	8·34
Sodium carbonate	0·35	0·49
Potassium sulphate	0·44	2·82
Potassium chloride	1·08	1·08
Insoluble	0·02	0·02
Water	16·29	0·58
	100·00	100·00
Total Alkalinity	100·37	115·74

CAUSTIC POTASH SOLUTION.—Liquor kali caustici pur.: pure potash solution (KOH + aq.). Clear, colourless solution. Sp. gr., 1·30. Containing about 33 per cent. KOH.

Test as under "Potassium Hydrate, pure by Alcohol," p. 258.

For sp. gr. of various strengths of solution, see table, p. 261.

POTASSIUM IODATE.—Kalium iodicum, puriss.: neutral iodate of potash (KIO_3). Mol. wt., 214·02. White cubic crystals. Soluble in water (1 : 14).

Tests for Impurities.—The salt must contain 100 per cent. KIO_3, give a clear solution with water, and show no acid reaction—i.e., no liberation of iodine must take place on addition of potassium iodide. About 0·5 gm. of the iodate is dissolved in about 20 c.c. of freshly boiled water and a small crystal of potassium iodide added, with a few drops freshly-prepared starch solution; the solution must not turn blue at once.

Note.—On standing for a short time, a blue colour always appears owing to atmospheric influence. See note under "Potassium Iodide".

Quantitative Estimation.—The iodic anhydride is calculated from the iodine liberated on addition of hydrochloric acid and potassium iodide, as under "Potassium Biniodate," p. 236.

Specific Gravity of Caustic Potash Solution at 15° (Lunge).

Sp. gr.	°B.	°Tw.	100 parts by weight contain		1 cbm. contains kilograms	
			K_2O.	KOH.	K_2O.	KOH.
1·007	1	1·4	0·7	0·9	7	9
1·014	2	2·8	1·4	1·7	14	17
1·022	3	4·4	2·2	2·6	22	26
1·029	4	5·8	2·9	3·5	30	36
1·037	5	7·4	3·8	4·5	39	46
1·045	6	9·0	4·7	5·6	49	58
1·052	7	10·4	5·4	6·4	57	67
1·060	8	12·0	6·2	7·4	66	78
1·067	9	13·4	6·9	8·2	74	88
1·075	10	15·0	7·7	9·2	83	99
1·083	11	16·6	8·5	10·1	92	109
1·091	12	18·2	9·2	10·9	100	119
1·100	13	20·0	10·1	12·0	111	132
1·108	14	21·6	10·8	12·9	119	143
1·116	15	23·2	11·6	13·8	129	153
1·125	16	25·0	12·4	14·8	140	167
1·134	17	26·8	13·2	15·7	150	178
1·142	18	28·4	13·9	16·5	159	188
1·152	19	30·4	14·8	17·6	170	203
1·162	20	32·4	15·6	18·6	181	216
1·171	21	34·2	16·4	19·5	192	228
1·180	22	36·0	17·2	20·5	203	242
1·190	23	38·0	18·0	21·4	214	255
1·200	24	40·0	18·8	22·4	226	269
1·210	25	42·0	19·6	23·3	237	282
1·220	26	44·0	20·3	24·2	248	295
1·231	27	46·2	21·1	25·1	260	309
1·241	28	48·2	21·9	26·1	272	324
1·252	29	50·4	22·7	27·0	284	338
1·263	30	52·6	23·5	28·0	297	353
1·274	31	54·8	24·2	28·9	308	368
1·285	32	57·0	25·0	29·8	321	385
1·297	33	59·4	25·8	30·7	335	398
1·308	34	61·6	26·7	31·8	349	416
1·320	35	64·0	27·5	32·7	363	432
1·332	36	66·4	28·3	33·7	377	449
1·345	37	69·0	29·3	34·9	394	469
1·357	38	71·4	30·2	35·9	410	487
1·370	39	74·0	31·0	36·9	425	506
1·383	40	76·6	31·8	37·8	440	522
1·397	41	79·4	32·7	38·9	457	543
1·410	42	82·0	33·5	39·9	472	563
1·424	43	84·8	34·4	40·9	490	582
1·438	44	87·6	35·4	42·1	509	605
1·453	45	90·6	36·5	43·4	530	631
1·468	46	93·6	37·5	44·6	549	655
1·483	47	96·6	38·5	45·8	571	679
1·498	48	99·6	39·6	47·1	593	706
1·514	49	102·8	40·6	48·3	615	731
1·530	50	106·0	41·5	49·4	635	756
1·546	51	109·2	42·5	50·6	655	779
1·563	52	112·6	43·6	51·9	681	811
1·580	53	116·0	44·7	53·2	706	840
1·597	54	119·4	45·8	54·5	731	870
1·615	55	123·0	47·0	55·9	754	902
1·634	56	126·8	48·3	57·5	789	940

Uses.—This salt has been recommended for standardising the standard sodium thiosulphate solutions, in place of iodine (Gröger, "Yearbook of Pharmacy," 1891, p. 140). On the preparation of potassium iodate and starch paper as a recognised test for free sulphuric acid, see "Pharm. Ztg.," 1896, p. 533.

Commercial Varieties.—These are often impure, and contain the iodide.

POTASSIUM HYDROGEN ANTIMONIATE.—See "Potassium Pyroantimoniate".

POTASSIUM IODIDE.—Kalium iodatum, puriss.: iodide of potassium (KI). Mol. wt., 166·02. White, crystalline cubes, easily soluble in water (2 : 1·4) or alcohol, and non-hygroscopic.

Note.—When kept for a long time the salt undergoes change, assuming a yellowish colour, the perfectly neutral iodide showing the colour sooner than that which contains free alkali.

Biltz ("Notizen zur Pharm. Germ.," p. 178) concludes that this is caused by oxidation (see also "Pharm. Ztg.," 1897, pp. 7, 77).

Tests for Impurities.—*Potassium Carbonate.*—When the salt is powdered and placed on moist red litmus paper the appearance of a violet-blue colour must not take place immediately.

Note.—Biltz (loc. cit.) states that iodide containing more than 0·1 per cent. K_2CO_3 shows this reaction at once.

Metals, Sulphuric Acid, Potassium Cyanide.—The aqueous solution (1 : 20) must show no reaction with either hydrogen sulphide or barium chloride; nor must a blue colour appear on adding a trace of ferrous sulphate, 1 drop of ferric chloride, then heating with caustic soda solution, and finally acidifying with hydrochloric acid.

Iodates.—A freshly-prepared solution in cold boiled distilled water must not be coloured immediately on addition of starch solution and dilute sulphuric acid.

Note.—J. Mühe ("Pharm. Central.," 27, p. 55 *et seq.*) insists on the use of perfectly pure sulphuric acid, well-boiled water, and neutral starch solution in conducting this test; according to this observer, distilled water containing carbonic acid and air decomposes the iodide with liberation of iodine. Regarding this reaction, H. Beckhurts ("J.C.S.," 1886, A., pp. 783, 834) states that the appearance of a blue

colour must on no account be taken as showing the presence of iodate, as the colour may be caused by chlorate and bromate, these compounds being formed from iodine chloride or bromide in presence of alkali in excess. Iodine chloride and iodine bromide are often present in the iodine used in the manufacture of iodide. The salt used in the preparation of standard iodine solutions must not contain iodic acid. As this is very important, the following method may be recommended as a check: On adding pure potassium iodide to dilute sulphuric acid the salt dissolves quickly and without producing any colour, but if iodate is present the solution becomes coloured through liberation of iodine. Fresenius adopts this method in his work on quantitative analysis in testing the iodide. Biltz ("Notizen zur Pharm. Germ.," p. 182) insists that the solution (1 : 20) should not give the slightest yellow colour with dilute sulphuric acid.

Nitric Acid.—1 gm. of the sample heated with 5 c.c. of caustic soda solution and 0·5 gm. zinc filings and iron powder must emit no smell of ammonia.

Note.—As the tests prescribed by the Second German Pharmacopœia have repeatedly led to errors, the above test is taken from the Third Pharmacopœia (see articles by L. Scholvien, "Rep. d. Chem.-Ztg.," 1887, p. 256, and C. Schwarz, "Rep. d. Chem.-Ztg.," 1888, p. 282). Schwarz recommends a further test for nitrates, but Scholvien states that commercial samples rarely contain nitric acid.

Chlorides and Bromides.—Silver nitrate is added to a solution of the salt until no further precipitate forms; ammonia is then added in excess, the mixture is shaken and filtered, and the filtrate acidified with nitric acid; the formation of a white, cheese-like precipitate indicates the presence of the above impurities.

Note.—On the testing of iodides for chlorides and bromides, see also "Hydriodic Acid," and "Iodine," and on the separation of iodide from chloride and bromide, see below.

Quantitative Estimation.—In estimating iodine and separating chlorine and bromine, it is advisable to use the distillation method with ferric chloride, iodides being decomposed with liberation of iodine by ferric chloride, or a ferric compound and hydrochloric acid, the chlorides and bromides remaining unchanged. The iodine is retained by a solution of potassium iodide, and then titrated with $\frac{n}{10}$ sodium thiosulphate (see "Iodine"). The method is described in detail in works on volumetric analysis. Topf ("J.C.S.," 1887, A., p. 997) describes

a new and good form of apparatus for the distillation. The iodine in the iodide can also be estimated gravimetrically with palladium dichloride (see "Iodine").

Note.—The solution of the neutral potassium iodide of commerce has a natural tendency to decompose more quickly, and become coloured sooner than the slightly alkaline salt. A trace of alkali (0·01 per cent.) may, therefore, be added to the solution, thus preventing the decomposing effect of carbonic acid in solution.

Uses and Storage.—The salt is used as a solvent for iodine in the preparation of standard iodine solutions, and further as an absorbent for chlorine; for such purposes it must be free from iodate in particular, and also practically free from carbonate. It is also employed as a test for metals, and in the preparation of Nessler's solution. It must be kept in a dark, dry place in glass-stoppered bottles with well-fitting stoppers.

Commercial Varieties.—These sometimes contain iodate and traces of carbonate and chloride. According to Biltz's experience, the best commercial samples rarely contain more than a quarter per cent. of KCl. Daudt ("Pharm. Ztg.," 1888, p. 117) has detected sulphites in the commercial iodide, and the hydrogen evolved on treating this sample with zinc and hydrochloric acid, coloured lead paper an intense black. Very pure iodide of good appearance can now be had from various sources. M. P. Carles ("Journ. de Pharm. et de Chimie," No. 10, Nov. 15th, 1891) gives analyses of eight commercial samples (see also C. Krauch, "Essais de pureté des réactifs chimiques," edition française par J. Delaite, Liége, 1892).

POTASSIO-IODIDE OF BISMUTH AND POTASSIO-IODIDE OF ZINC.

Alkaloid Reagents.—These double iodides cause the precipitation of the alkaloids, and are therefore used for their detection; their method of preparation is given in the appendix. They are sold both in the crystalline form and in solution, and are tested after the same method as the simple salt (e.g., cadmium iodide) and must give the well-known precipitation above mentioned.

POTASSIO-IODIDE OF CADMIUM AND POTASSIO-MERCURIC-IODIDE.

POTASSIUM MANGANATE.—Kalium manganic.: manganate of potash (K_2MnO_4). Mol. wt., 197·13. The preparation, which is deep green and strongly alkaline, is obtained by fusing pure permanganate of potash with pure caustic potash, but is seldom used in analysis (Jolles, "J.S.C.I.," 1889, p. 819).

POTASSIUM NITRATE.—Potassium nitricum puriss.: nitrate of potash (KNO_3). Mol. wt., 101·11. Colourless rhombic crystals, or crystalline powder, dry and non-hygroscopic, easily soluble in water (1 : 4).

Tests for Impurities.—*Solubility, Lime, Heavy Metals, etc.*—3 gms. in 50 c.c. of water must give a clear neutral solution, and no change should take place on adding ammonia, oxalate of ammonium and ammonium sulphide. The aqueous solution, acidified with a little hydrochloric acid, should show no change on addition of hydrogen sulphide.

Chlorides and Chlorates.—The solution (1 : 20) must show no reaction with silver nitrate. On slightly igniting 1 gm., dissolving in water (1 : 20), and adding a few drops of nitric acid, the addition of silver nitrate must again show no reaction.

Note.—Perchlorate: Haüssermann ("Chem.-Ztg.," 1894, p. 1206, and "J.S.C.I.," 1894, p. 947) calls attention to the presence of perchlorate. On heating a nitrate containing this impurity with excess of sulphuric acid, and distilling, a normal distillate containing but little chlorine was at first obtained, but, towards the end of the distillation, the presence of an acid, giving a copious precipitate of the chloride with silver nitrate was detected.

Panaotovié ("Chem.-Ztg.," 1894, p. 1567; "J.S.C.I.," 1895, p. 157) found that out of 180 barrels of saltpetre, obtained two years previously from a well-known firm, 122 contained more than 0·25 per cent. perchlorate, a few even containing over 1 per cent. Ruer ("D.R.-P.," 81, 102) recommends crystallising the raw saltpetre from water, and then evaporating the solution of the salt to dryness and fusing in order to destroy the perchlorate. On the estimation of perchlorate in saltpetre, see also Winteler ("J.S.C.I.," 1897, p. 358), who found 0·27 per cent. in a pure sample.

Sodium.—Test as under "Potassium Carbonate," p. 242.

Sulphates.—A solution of 3 gms. in 60 c.c. of water must show no reaction with barium chloride, even after standing for several hours in a warm place.

Quantitative Estimation.—The salt is sold in such a pure

condition that a quantitative estimation is generally superfluous. When necessary it may be made according to Fresenius, "Quant. Anal.," vol. i., p. 390.

In valuing commercial saltpetre, an estimation of the percentage of sodium chloride present constitutes nearly all the testing required. Manufacturers generally guarantee a maximum of so many parts NaCl present (e.g. 1 part in 10,000, or 0·01 per cent. NaCl); this may be checked by titrating 10 gms. with $\frac{n}{10}$ silver nitrate.

Uses.—Potassium and sodium nitrates are used as oxidising agents, as in the estimation of chlorine and sulphur in organic substances; in this case the nitrates must be free from these elements. In forensic chemical analysis, saltpetre, and particularly sodium nitrate (described later on), are used for destroying organic substances in the hydrogen sulphide precipitate and various other organic residues, and also for the oxidation of metallic sulphides. The salts must therefore be absolutely free from poisonous metals. Saltpetre, or nitre as it is sometimes called, is used in inorganic analysis for the conversion of the sulphides of tin, antimony, and arsenic into their acids and oxides, and for the detection of chromium and manganese.

Commercial Varieties.—A commercial saltpetre, containing traces of sodium chloride, but otherwise practically pure, can be obtained (see under "Quantitative Estimation").

POTASSIUM NITRITE.—Kalium nitros. puriss.: nitrite of potash (KNO_2). Mol. wt., 85·17. Short pencils, white, or very slightly yellow, extremely hygroscopic, and containing about 90 per cent. of the salt. Easily soluble in water (1 : 1·5).

Tests for Impurities.—*Heavy Metals.*—Addition of ammonium sulphide must produce no precipitate in the aqueous solution (1 : 20).

Note.—Tests may be made for free alkali, potassium carbonate, chlorides, sulphates, and nitrates, traces of which are always present, but the quantitative estimation of the nitrite generally renders the qualitative tests superfluous.

Quantitative Estimation.—In practice this is generally conducted as follows, according to Feldhaus: A permanganate solution standardised on silver nitrite or iron is added from

a burette to a very dilute acidified solution of the nitrite until the pink colour remains permanent; the percentage is then calculated from the amount of permanganate used. Lunge considers this method inaccurate, and that it is much better to reverse the process by adding the nitrite solution from a burette to a known quantity of acidified permanganate until the pink colour just disappears ("Zeit. f. angew. Chem.," 1891, p. 629). This method may be advantageously employed. For the estimation of either potassium or sodium nitrite the procedure is as follows: A permanganate solution containing 15·80 gms. of the purest potassium permanganate per litre is first prepared—1 c.c. = 0·02792 gm. iron, 0·0315 gm. crystallised oxalic acid, and ·0213 gm. of KNO_3 or 0·01725 gm. $NaNO_2$. The oxidation of nitrite to nitrate takes place according to the following equation:—

$$2KMnO_4 + 5NaNO_2 + H_2O = 5NaNO_3 + 2MnO + 2KOH.$$

For the estimation, 10 gms. of the nitrite are dissolved in a litre of water, and this solution added from a burette in a thin stream to 20 c.c. $\frac{n}{2}$ permanganate, which has been diluted with 130 c.c. of water previously heated to 40° and acidified with sulphuric acid until the permanganate is decolorised on standing for a short time.[1]

Note.—It may be remarked that Lunge has found the so-called sulphanilic acid method, and also the aniline method, to give unreliable results. A. G. Green and F. Evershed ("Chem. News," 1892, 65, p. 109) on the contrary find the latter to give good results according to their experience. This method is based on the formation of a diazo compound when titrating with a normal solution of aniline hydrochloride, using starch and zinc iodide as indicator. Lunge, in reply to the article by these authors, again insists on the superiority of the permanganate method.

Uses and Storage.—The salt is used in the estimation of cobalt, and for the liberation of iodine from its compounds; also for the estimation of amido acids, for which purpose it is sometimes necessary to remove the traces of carbonate nearly

[1] When silver nitrite is tested by Lunge's method, the salt must be dissolved in a certain volume of the purest concentrated sulphuric acid, taking care that no oxides of nitrogen are allowed to escape, and the nitro-sulphuric acid thus formed run into the permanganate solution, as above.

always present in the commercial salt. In order to effect this V. Kreussler recommends adding calcium nitrate to the concentrated solution of the nitrite so long as a precipitate forms. The latter is then rendered crystalline by applying slight heat, and the solution filtered off. The solution thus obtained contains potassium nitrate, which, however, does not interfere with the above estimation. The nitrite has also been recommended by Campain for the determination of urea.

Owing to its hygroscopic nature, the salt must be carefully stored in well-closed vessels.

Commercial Varieties.—The author is not aware that it is possible to obtain samples in the trade containing 100 per cent., as the preparation of such an article would be very difficult. Samples containing 80 to 90 per cent. are, however, more easily obtainable, and the purest form of nitrite may be expected to contain the latter percentage. Some manufacturers sell as a specially pure nitrite a quality which barely contains 70 per cent., a fact to which the author desires to call special attention, as he believes that the matter has not yet been commented upon in any literature on the subject.

POTASSIUM OXALATE, NEUTRAL.—Kalium oxalic. neutrale, puriss. ($C_2O_4K_2$, H_2O). Mol. wt., 184·22. Easily soluble crystals (1 : 3·5 water at 0°), which effloresce on heating, and show a neutral reaction.

Tests for Impurities and Quantitative Estimation.—See under "Ammonium Oxalate," p. 34.

The estimation by titration with permanganate is described in Fresenius, "Quant. Anal.," vol. i., p. 324.

Uses.—Among other applications, the salt is used for the testing of quinine (Allen's "Comm. Organ. Anal.," vol. iii., pt. ii., p. 417).

Commercial Varieties.—These are sometimes found containing distinct traces of chlorides, sulphates, and lead.

POTASSIUM PERCHLORATE. — Kalium perchloricum : perchlorate of potash ($KClO_4$). Mol. wt., 138·47. Colourless crystalline powder (rhombic), soluble in about 50 parts of water.

Tests for Impurities.—As under "Potassium Chlorate," p. 244.

Quantitative Estimation.—Hydrochloric acid does not decompose the perchlorate, and the estimation of perchloric acid in its salts is not, as a general rule, made directly, the amount present being usually calculated from the estimation of the base. Another method is to calculate from the chloride remaining after ignition of the salt, a method only applicable, however, when the perchlorate is free from chlorides. These methods are not accurate, and Kreider recommends a new and reliable process, based on the fact that the oxygen evolved during ignition may be retained by a mixture of nitric oxide and concentrated hydriodic acid, and the iodine thus liberated titrated with $\frac{n}{10}$ arsenious acid. For details of this method, see Kreider, "J.S.C.I.," 1896, p. 473.

Uses.—The salt is formed by carefully igniting the chlorate till the mass, at first rather inclined to liquefy, has become pasty and viscous; it is then purified with water. It sometimes replaces the chlorate in ultimate organic analysis.

Commercial Varieties.—These often contain the chloride.

POTASSIUM PERIODATE (KIO_4).—Was recommended by H. H. Willard and L. H. Greathouse ("J. Amer. Chem. Soc," 1917, 39, pp. 2366-2377), for the colorimetric estimation of manganese which it oxidises to permanganate.

POTASSIUM PERMANGANATE.—Kalium permanganicum, pur.: permanganate of potash ($KMnO_4$). Mol. wt., 157·94. Dry rhombic crystals of a deep purple colour and metallic lustre, completely soluble in water (1 : 15), and neutral in dilute solution.

Tests for Impurities.—*Sulphates and Chlorides*—On heating to boiling 0·5 gm. of the salt with 2 c.c. of alcohol and 25 c.c. of water, a colourless filtrate should be obtained which, after acidifying with nitric acid, must show only a slight opalescence with barium nitrate and silver nitrate ("Pharm. Germ.," iii.) respectively.

Nitrates.—On slowly adding oxalic acid to a solution of 0·5 gm. in 5 c.c. of hot water until the pink colour has disappeared,

and filtering, 2 c.c. of the clear filtrate with 2 c.c. of sulphuric acid must not show a coloured ring on slowly pouring in 1 c.c. of ferrous sulphate solution ("Pharm. Germ.," iii.).

The salt must contain 99 to 100 per cent. $KMnO_4$.

Quantitative Estimation.—For the estimation 2 gms. are dissolved in pure distilled water, and the solution made up to 1 litre. A solution of 39·14 gms. pure ferrous-ammonium sulphate in 1000 c.c. of recently boiled distilled water is next prepared; 10 c.c. are then drawn off, and a little sulphuric acid added; the permanganate solution is now added from a burette until the pink colour remains. In 10 c.c. of the solution of iron salt there is present 0·05584 gm. Fe, equivalent to 0·03159 gm. $KMnO_4$ (Fe × 0·5657 = $KMnO_4$); therefore the amount of permanganate added ought to contain 0·03159 gm. $KMnO_4$. The percentage of pure salt in the sample may easily be found by dividing the factor 0·03159 by the amount of permanganate present in the number of c.c. used.

In place of the double iron salt, oxalic acid may be used, 1 gm. of potassium permanganate being equivalent to 1·995 gms. oxalic acid, deduced from the equation :—

$$5(C_2H_2O_4,\ 2H_2O) + 3H_2SO_4 + 2KMnO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 18H_2O.$$

1 c.c. $\frac{n}{2}$ oxalic acid (31·515 gms. crystallised acid per litre) is equal to 0·015794 gm. $KMnO_4$ (see under "Oxalic Acid"; also Fresenius, "Quant. Anal.," vol. i., p. 217 *et seq.*).

Note.—The salt may be accurately estimated by the nitrometer, a method which is also useful for standardising the permanganate solution. In presence of hydrogen peroxide, decomposition takes place according to the equation :—

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 10O + 8H_2O + 2MnSO_4 + K_2SO_4.$$

The volume of oxygen liberated is measured, and the percentage of permanganate calculated. Lunge's experience goes to prove the accuracy of this method (see "J.S.C.I.," 1890, p. 21). Those not sufficiently familiar with gas volumetric analysis may with advantage adopt the foregoing methods with iron and oxalic acid. A detailed description of the nitrometer may be found in Lunge's "Manufacture of Sulphuric Acid and Alkali," vol. i., p. 182 *et seq.* and in nearly all works on commercial analysis.

Uses and Storage.—On account of its importance as an oxidising agent the salt is much used in analytical work. For

the quantitative estimation of sulphur it must be free from H_2SO_4; this special preparation, described in the following article, should be used in making standard solutions, as it contains 100 per cent. $KMnO_4$.

The salt is chiefly used in the preparation of standard solutions. Fresenius ("Quant. Anal.," vol. i., p. 215) uses a solution of 5 gms. per litre, which he subsequently standardises. The decinormal solution, so frequently used, is made by dissolving 3·16 gms. to 1 litre, and is so standardised that each c.c. equals 0·0056 gm. Fe. The solution is standardised on pure iron wire, iron double salt, oxalic acid, or its salts, and the methods are exhaustively treated of in Sutton, "Vol. Anal.," 7th ed., p. 121 *et seq.*; also under "Potassium Tetroxalate," p. 276. Sutton also describes the nitrometer method. On the detection of cocaine, etc., by means of potassium permanganate, see E. H. Hankin, "Analyst," 1911, 36, pp. 1-6.

Regarding the keeping qualities of the solution, Poleck ("Chem.-Ztg.," 1892, p. 908) remarks that solutions of 1 to 3 parts per 1000 remain unchanged for about a year if protected from dust and kept in the dark. Grützner ("Arch. d. Pharm.," vol. ccxxxi., p. 320) records an instance of a 0·3 per cent. solution remaining perfectly unaltered after keeping in a stoppered bottle for one year and a half, whereas a solution of 1 in 1000 had lost 2·61 per cent.

Permanganate of potash, both in the solid state and in solution, must be well protected from light, dust, and organic matter.

Commercial Varieties.—Two qualities—one in large, the other in small, crystals—may be obtained, and both of such purity that they easily conform to the specification of the "Pharm. Germ.," iii. The preparation, free from sulphuric acid, is sold for special analytical purposes. A crude potassium permanganate of inferior quality and consisting chiefly of manganate can also be obtained.

POTASSIUM PERMANGANATE, FREE FROM SULPHURIC ACID.—Large, deep purple crystals, containing about 100 per cent. $KMnO_4$.

Tests for Impurities.—*Sulphuric Acid.*—On heating 3

gms. in 150 c.c. of water, and 15 c.c. of alcohol, until the solution is completely reduced, the colourless filtrate, after acidifying with a few drops of acetic acid and adding barium chloride, must show no reaction, even after several hours.

Chlorides and Nitrates.—As given on p. 269.

Quantitative Estimation.—See p. 270.

POTASSIUM PERSULPHATE.—Kalium persulfuricum, $K_2S_2O_8$. Mol. wt., 270·32. White crystals soluble in about 50 parts of water.

Uses.—Is employed in the fusion and oxidation of the ores of chromium, cadmium, iron, manganese, copper, etc. (Merck's "Index," p. 284). For the action of potassium persulphate on quinol, aniline, etc., see R. L. Datta and J. N. Sen., "J. Amer. Chem. Soc.," 1917, pp. 747-750.

On the detection of persulphates, perborates, percarbonates, and periodic acid, see W. Lenz and E. Richter, "Z. anal. Chem.," 1911, 50, pp. 537-544; "J.S.C.I.," 1911, p. 1010.

Ammonium persulphate is recommended for the estimation of small quantities of manganese (H. Lührig, "Chem. Zeit.," 1914, 38, pp. 781-783; "J.S.C.I.," 1914, p. 709).

POTASSIUM PYROANTIMONIATE (ACID).—Kalium stibicum, pur. ($K_2H_2Sb_2O_7$, $6H_2O$). Mol. wt., 540·71. White, granular, crystalline powder, difficultly soluble in cold water (1 : 250), soluble in hot water (1 : 90).

Tests for Impurities.—*Nitric Acid, etc.*—The solution (1 : 250) must be neutral to litmus paper, and, on mixing with an equal volume of sulphuric acid and carefully adding ferrous sulphate solution, a brown ring must not appear at the juncture of the liquids. The solution, freshly prepared, must give a crystalline precipitate with sodium chloride, but none with potassium or ammonium chloride.

Quantitative Estimation.—The salt is dissolved in hydrochloric acid, tartaric acid added, and the antimony precipitated from the dilute solution with hydrogen sulphide (see Fresenius, "Quant. Anal.," vol. i., p. 272). The filtrate from the antimony sulphide is evaporated to dryness, ignited, neutralised with hydrochloric acid, and the potash estimated with platinum bichloride.

Uses.—The salt in solution is used for the detection of sodium salts, but the test must be very carefully conducted, since the solution under examination must only show a neutral or slightly alkaline reaction; also, the solution must not be too dilute, and must not contain bases other than potash or soda. The solution of the salt must only be made shortly before use, and should be prepared by boiling with water and filtering off from the undissolved salt.

Commercial Varieties.—These generally contain a large quantity of saltpetre.

POTASSIUM SODIUM TARTRATE. — Rochelle salt, $KNaC_4H_4O_6 + 4H_2O$. Mol. wt., 282·22. White crystalline salt (rhombic prisms). Easily soluble in water (1 : 1·7).

Preparation.—The double tartrate of potassium and sodium is prepared by exactly neutralising potassium hydrogen tartrate ($KHC_4H_4O_6$) with sodium carbonate, boiling and crystallising out.

Tests for Impurities.—When added to a solution of copper sulphate and heated it should give no reduction (see Fehling's solution p. 108).

POTASSIUM SULPHATE.—Kalium sulphuricum, puriss.: sulphate of potash (K_2SO_4). Mol. wt., 174·26. Fine, white rhombic crystals, giving a clear solution with water (1 : 10).

Tests for Impurities.—*Chlorides, Metals, etc.*—The aqueous solution (1 : 20) must be clear and neutral, and must give no reaction with hydrogen sulphide water, ammonium oxalate and potassium carbonate, or silver nitrate.

Sodium.—When heated on platinum wire, no yellow flame must be apparent.

Ammonia.—A solution of 10 gms. of the material should give no colour with Nessler's solution.

Quantitative Estimation.—As under "Potassium Bisulphate".

Uses.—The salt is sometimes used to precipitate barium from its compounds, also in the Kjeldahl nitrogen process.

Commercial Varieties.—Preparations for technical purposes, often containing sodium sulphate, potassium chloride, arsenic,

and free acid, are also obtainable. On the testing of commercial samples, see Böckmann, "Chem.-techn. Untersuch.," 3rd ed., p. 502.

POTASSIUM SULPHIDE.—Kalium sulphurat. pur. e Kali carb. pur.

Pure liver of sulphur is prepared by heating carefully 1 part of pure sulphur with 2 parts of pure potassium carbonate, the resulting mixture consisting chiefly of potassium tersulphide and potassium thiosulphate. As the salt is used in the Kjeldahl process the potassium carbonate used must be free from nitrogen. The compound is sold in the form of leather brown lumps or grains, giving a clear solution with water; on adding acetic acid in excess a copious evolution of hydrogen sulphide ensues.

POTASSIUM SULPHYDRATE.—Kalium sulphydrat. cryst. puriss. ($(KSH)_2$, H_2O). Mol. wt., 162·33. Crystalline mass, hygroscopic and colourless, or only faintly coloured, readily soluble in water, also soluble in alcohol. The solution dissolves sulphur with evolution of hydrogen sulphide.

Tests for Impurities.—*Appearance.*—As above.

Polysulphides.—Acids should give a copious evolution of H_2S without liberating sulphur; no objection must be taken, however, to a slight opalescence on adding acid, nor to a slightly coloured solution of the salt alone.

Storage.—Polysulphides are soon formed on oxidation by the air, the salt becoming yellow (see also "Ammonium Sulphide," p. 37), and, on adding acid, sulphur is at once precipitated. During storage slight decomposition cannot be avoided, even under the most favourable conditions.

POTASSIUM SULPHYDRATE SOLUTION.—Potassium sulphydrat. puriss. solut. A colourless liquid; tests and storage as above.

POTASSIUM MONOSULPHIDE SOLUTION. — Kalium monosulphurat. puriss. solut.: solution of monosulphide of potassium (K_2S). Mol. wt., 110·26.

A quantity of pure nitrogen-free caustic potash solution is first prepared; this solution is then divided into two equal por-

tions; hydrogen sulphide is passed through one portion till saturated, when it is then mixed with the other to form the above solution. The preparation is similar to that described under "Ammonium Sulphide," p. 36; it must be colourless, and give a copious evolution of hydrogen sulphide with acids without precipitation of sulphur, and must dissolve sulphur without liberating the above gas, in contradistinction to the hydrosulphide. The liquid, like ammonium sulphide, readily assumes a yellow colour on keeping through access of air, and when this has occurred the addition of acid precipitates sulphur. The same precautions must be adopted in storage.

POTASSIUM SULPHOCYANIDE.—Kalium rhodonatum, puriss. cryst. (CNSK). Mol. wt., 97·17. White crystals, giving a clear solution with water or warm absolute alcohol (1 : 10).

Tests for Impurities.—*Solubility.*—See above.

Sulphates.—The aqueous solution (1 : 20) must show no reaction with barium chloride within 5 minutes.

Iron.—The solution (1 : 20) must show absolutely no colour on addition of a little hydrochloric acid (1·19 sp. gr.) diluted with 10 c.c. of water.

Other Heavy Metals.—The solution (1 : 20) must neither show a precipitate nor a brown coloration with ammonium sulphide.

Ammonia.—The aqueous solution, on being warmed with excess of caustic potash, should evolve no alkaline vapour.

Quantitative Estimation, Uses, etc.—See under "Ammonium Sulphocyanide".

The bottles containing the salt must be well stoppered.

Sulphocyanide Paper is used for demonstrating the presence of hydrochloric acid in the contents of the stomach, and may be prepared by adding iron acetate solution to a 10 per cent. solution of the sulphocyanide, and dipping filter paper into the mixture (see p. 144).

Commercial Varieties.—Several qualities are found on the market. In even the purest commercial samples the author has detected traces of iron and lead, but for analytical purposes the salt must be perfectly free from such impurities, and have a fine, white appearance.

POTASSIUM TETROXALATE. — Kalium tetraoxalicum, puriss. ($HKC_2O_4 + H_2C_2O_4, 2H_2O$). Mol. wt., 254·09. Small white crystals giving a clear solution with water (1 : 33).

Tests for Impurities.—*Sulphuric Acid and Metals.*—As under "Ammonium Oxalate," p. 34. The composition of the salt may be found volumetrically by titration with normal potash, and with potassium permanganate as a check. The salt must contain 100 per cent. The crystals must be so carefully dried that on shaking up in a dry glass no particles adhere to the sides.

Quantitative Estimation.—The solution is titrated with normal alkali, as above mentioned; 1 c.c. normal caustic potash equals 0·06352 gm. crystallised oxalic acid, or 0·0845 gm. potassium tetroxalate, using litmus as indicator. To check this method the solution may be titrated with permanganate according to the following equation:—

$$10(HKC_2O_4 + H_2C_2O_4, 2H_2O) + 8KMnO_4 + 17H_2SO_4 = 40CO_2 + 8MnSO_4 + 9K_2SO_4 + 52H_2O.$$

2540·9 parts by weight of potassium tetroxalate are equal to 1263·52 parts by weight of potassium permanganate, or 1 part permanganate equals 2·011 parts tetroxalate. The permanganate is standardised on carefully dried oxalic acid (*q.v.*) or ammonium oxalate. The tetroxalate multiplied by 0·9922 is equal to oxalic acid, or for 1 gm. tetroxalate 0·9922 gm. oxalic acid must be found if the salt contains 100 per cent. The method of titration is described under "Oxalic Acid" (see also Fresenius, "Quant. Anal.," vol. i., p. 324).

Uses and Storage.—Ulbricht ("Pharm. Central.," 26, pp. 198-199) recommends the salt as a good permanent standard in volumetric analysis for standardising permanganate solutions, as well as a general standard in alkalimetry and acidimetry. Krant previously recommended the salt for that purpose ("Zeit. f. anal. Chem.," 26, pp. 350, 629). It has recently been observed that the preparation of the pure salt presents difficulties, owing, as it has been said, to the presence of water contained in the crystals causing the salt to effloresce, and it must therefore be both carefully prepared and dried at not too high a temperature, and must be kept in the dark in well-stoppered bottles.

Commercial Varieties.—Parsons ("Chem. Centralblatt," 1892, 2, p. 896) mentions that he has found some very impure tetroxalate in commerce.

POTASSIUM TIN-SULPHATE. — *Kalium Stanno-Sulphuricum*, $K_2Sn(SO_4)_2$. Mol. wt., 389·02. White crystals soluble in solutions of the alkalies and in hydrochloric acid.

Uses.—Employed as a reagent for mercury and bismuth salts, also for the volumetric estimation of nitric acid by the method of Lougi (Merck's "Index," p. 284).

PYRIDINE.—Pyridin. C_6H_5N. Mol. wt., 91·08. Colourless highly refractive liquid. Sp. gr., 0·982. B.p., 116°-118°. Miscible with water in all proportions but thrown out of solution on addition of NaHO. Also mixes readily with alcohol and ether.

Uses.—Forms a good solvent for resinous matter and has lately come into prominence as a reagent for the separation of the constituents of coal.

Pyridine may also be used for the quantitative separation of iron from aluminium (J. A. Sanchez, "Bull. Soc. Chim.," 1911, 9, pp. 880-881; "J.S.C.I.," 1911, p. 1283).

PYROGALLIC ACID.—Acid pyrogallic, bisublimat.: pyrogallol ($C_6H_3(OH)_3$). Mol. wt., 126·081. Light, white crystalline flakes, or lustrous needles. M.p., 131°. Easily soluble in water and alcohol.

Tests for Impurities.—*Solubility.*—A solution in 2 parts of water must be clear, colourless, and neutral; the solution in ether or alcohol must also be clear.

Residue.—On carefully heating 1 gm. the acid must sublime without leaving any residue.

Quantitative Estimation.—The tests given above, along with the melting point (131°), will be sufficient. Concerning the melting point of the acid, see "Pharm. Ztg.," 1897, p. 779. An aqueous solution quickly turns brown on adding caustic soda solution.

Uses and Storage.—An alkaline solution of the acid absorbs oxygen with avidity, and is used in gas analysis. Winkler prepares the following solution for this purpose: 50 gms. of pyrogallic acid are dissolved in a litre of caustic potash solution

of 1·20 sp. gr. 1 c.c. absorbs 13 c.c. of oxygen. It is of no advantage to use a strong solution of, say, 1·5 sp. gr. On the colour reactions of the acid with beetroot sugar, resorcin, orceïn, *a*-naphthol, etc., see "J.S.C.I.," 1887, p. 455, and on similar reactions of pyrogallic acid, phloroglucin, resorcin, indol, etc., with lignified cell structures, see "Rep. d. Chem. Ztg.," 1886, p. 268. It is also used as a delicate test for propeptone (see "J.C.S.," 1887, A., p. 1127), and its employment for the estimation of nitric and nitrous acids is described in "Analyst," x., p. 212.

Air must be carefully excluded during storage. In time the aqueous solution turns brown in contact with the atmosphere and shows an acid reaction. Some samples after exposure to light and air, even in the solid state, fail to give a neutral, colourless solution ("Arch. d. Pharm.," 1887, p. 97). Detailed notes regarding its solubility are also given in this reference.

Commercial Varieties.—The acid now sold has a beautiful appearance, and is in good condition generally.

PYROGALLOL DIMETHYLETHER.—A 2 per cent. solution of pyrogallol dimethylether is recommended by J. Meyerfield ("Chem. Zeit.," 1910, 34, p. 948; "J.S.C.I.," 1910, p. 1135) as a test for chromic acid, ferric salts, and nitrous acid, with which it gives a yellow or red coloration. It is capable of detecting ·000002 gram of chromic acid or ·000016 gram of potassium nitrite in 10 c.c. The reaction is also observed with dilute solutions of chlorine, bromine, and potassium permanganate but not with nitric acid, hydrogen peroxide, or free oxygen.

PYRROL (C_4H_4NH). Mol. wt., 67·07. A colourless liquid base, sp. gr. 0·975, boiling at 133°, insoluble in water, mixes with alcohol and ether in all proportions.

Ihl ("J.S.C.I.," 1891, p. 165) considers an alcoholic solution of this substance to excel in delicacy all known tests for lignin, not even excepting phloroglucin. In hydrochloric acid solution pyrrol shows a red colour in presence of any of the aldehydes, after warming slightly.

RESORCIN.—Resorcinum puriss. ($C_6H_4(OH)_2$). Mol. wt., 110·08. Colourless crystals, of faint peculiar odour, easily soluble in water (1 : 0·69) at 12·5°, alcohol, and ether. M.p., 110°-111°, distils at 276·5°

Note.—When the melting point is low, the substance has not been properly purified.

Tests for Impurities.—*Residue.*—A few grams of the substance must volatilise completely on heating.

Empyreumatic Substances, Acids and Phenol.—The aqueous solution must be colourless, neutral to litmus paper, and must not smell of phenol on heating.

The pure compound ought to be practically odourless.

Note.—According to Schoop ("Chem. Ind.," 1887, p. 487) the ordinary impurities present in commercial resorcin are water, other isomers and homologues such as pyrocatechin, hydroquinone, phloroglucin, etc., resinous matter, and phenol. Pyrocatechin may be precipitated with lead acetate. On heating with ferric chloride, the presence of hydroquinone may be detected through the solution smelling of quinone. Pinewood is coloured red in presence of phloroglucin, and Schoop tests for phenol by shaking the ethereal solution with a few drops of concentrated caustic soda solution, whereby the phenol is dissolved, and may be detected by the smell on acidifying the solution.

Melting Point.—See above. When absolutely anhydrous the compound melts at 119° C., that of the German Pharmacopœia (iii.) showing a melting point of from 110°-111°.

Quantitative Estimation.—The appearance, along with the tests given above, are generally sufficient evidence of the degree of purity, but where a quantitative estimation is required a solution of known strength is mixed with standard bromine solution and the excess of bromine estimated with sodium sulphite and potassium iodide in the usual way (Degener, "Journ. f. prakt. Chem.," pp. 220, 322). The estimation may also be made with normal potassium iodide (see Schoop, loc. cit.).

Uses and Storage.—The compound is of great service in many analytical investigations, and the following may be quoted as being among the most important :—

(1) As a test for chloral and chloroform (Léon Crismer, "Pharm. Ztg.," 1888, p. 651).

(2) For the detection of chloroform in ethyl bromide (Scholvien, "Pharm. Ztg.," 1891, p. 299, and "J.S.C.I.." 1891, p. 799).

(3) As a test for hydrochloric acid in the gastric juice ("Pharm. Ztg.," 1891, p. 393).

(4) For the detection of lignified tissue (Ihl, Warnecke, "Rep. d. Chem.-Ztg.," 1888, p. 268; Warnecke, "J.S.C.I.," 1888, p. 870).

(5) For the recognition of certain ethereal oils (Ihl, "J.S.C.I.," 1889 p. 421).

(6) For the detection of beet sugar and other carbohydrates (Ihl, "J.S.C.I.," 1887, p. 455).

(7) As a test for nitrates and nitrites (Liebermann, 1874, "Ber. d. d. chem. Ges."; Gutzkow, "Pharm. Ztg.," 1889, p. 560).

(8) In the colour reactions of some phenols with regard to their use for qualitative analysis.

(9) As a test for nitrates, according to Lindo, "J.C.S.," 1889, A., p. 75.

A solution of 1 gm. resorcin in 100 c.c. of water and 10 drops of sulphuric acid presents a delicate test for nitrous acid, having the advantage over Griess's meta-phenylene-diamine test of remaining stable in contact with the atmosphere ("Jour. Pharm. Chim.," 6 Sér., ii., p. 289). The compound must be protected from the light.

(10) As a test for zinc and copper (Merck's "Annual," 1910, p. 302).

(11) As a test for tartaric acid, along with strong sulphuric acid and heat it gives a rose red-colour which disappears on dilution with water.

Commercial Varieties.—White crystallised puriss., white resublimed, and the ordinary pure resorcin may all be obtained in a state of great purity. Commercial resorcin, a slightly coloured, dry, crystalline mass, may also be obtained fairly pure. The impurities of commercial varieties are treated of in the note under "Tests".

ROSOLIC ACID.—Bright green metallic crystals soluble in alkalies with a red colour, consisting chiefly of the compound $C_{20}H_{16}O_3$, isomeric with methylaurin, and homologous with aurin. It is pale yellow unaffected by acids but changed to violet-red by alkalies. On its use as an indicator, see Sutton's "Vol. Anal.," p. 38. Its degree of sensitiveness is described in the table, p. 142.

RUTHENIUM RED.—Formula $Ru_2(OH)_2Cl_4(NH_3)_7 + 3H_2O$. Soluble in water, insoluble in alcohol.

Uses.—Is employed as a staining medium for microscopic work. The strength of the solution being 0·1 gram in 100 c.c. (see F. J. G. Beltzer, "Monit. Scien.," 1911, 1, pp. 633-641; "J.S.C.I.," 1911, p. 1206).

SACHSSE'S SOLUTION.—Standard solution of mercuric iodide used in the estimation and differentiation of sugars.

This solution is prepared by dissolving 18 gms. of pure mercuric iodide and 25 grams of potassium iodide in 500 c.c. of distilled water. To this is added a solution of 80 gms. of caustic potash and the whole made up to 1 litre with distilled water.

SALICYLIC ACID. — Acid. salicylic. puriss. recryst., $C_6H_4(COOH)(OH)$. Mol. wt., 138·08. White, light, odourless crystals (monoclinic), soluble in about 300 parts of cold water, easily soluble in alcohol and ether. M.p., 156°-157°.

Tests for Impurities.—The acid must possess the above properties, and should not smell of phenol. A solution of 1 gm. in 10 c.c. of ether must be *clear* and colourless. On heating 0·5 gm. on platinum foil no residue must remain. The melting point should be 157°. A solution of 1 gm. in 6 gms. of concentrated sulphuric acid must be almost colourless. On dissolving 1 gm. in alcohol, adding a few drops of nitric acid and a little silver nitrate, no chlorine reaction must appear.

The residue obtained on spontaneous evaporation of the alcoholic solution should be perfectly white.

A solution of the acid neutralised with Na_2CO_3, shaken with ether and the ether evaporated, should leave little or no residue, and this should have no odour of phenol. For the

detection of p-hydroxybenzoic acid in salicylic acid, see E. Rupp and R. Loose ("Ber.," 1908, 41, pp. 3905-3908; "J.S.C.I.," 1908, p. 1223).

Uses.—Owing to its property of arresting fermentation, the acid is used in the laboratory as a preservative, and has also been proposed as an indicator (Allen's "Comm. Organ. Anal.," vol. iii., pt. i., p. 53). It is also used in the Kjeldahl process when the nitrogen of nitrates is to be estimated.

The most characteristic test for salicylic acid is the violet colour produced with ferric chloride in a neutral solution.

Note.—Salicyl-sulphonic acid is a white crystalline substance easily soluble in water, and is prepared by heating salicylic acid with sulphuric acid; it is used as a test for protein substances ("Pharm. Ztg.," 1892, p. 325; and Allen's "Comm. Organ. Anal.," vol. iv., p. 56).

Commercial Varieties.—The acid is now nearly always prepared synthetically, and may be obtained very pure.

SCHIFF'S REAGENT.—A general reagent for the detection of aldehydes. Is prepared by dissolving 0·5 gram of fuchsine (magenta) in 100 c.c. of water and decolorising by passing SO_2 through the solution then making up to 1 litre.

With aldehydes an immediate violet-red coloration is produced.

SILVER.—Argent. metallic. puriss. (Ag). At. wt., 107·88. Pure white metal in the form of sheets.

Tests for Impurities.—*Foreign Metals.*—The metal is dissolved in nitric acid, precipitated as chloride and the filtrate evaporated. If a residue remains it is dissolved in nitric acid and tested with hydrogen sulphide, ammonia, and ammonium sulphide.

Quantitative Estimation.—At all the Mints the silver is estimated by normal sodium chloride, a method introduced by Gay-Lussac, and more accurate than the former cupellation process, which showed a loss amounting to from 0·5 to 0·6 per cent., or even more. In using this method all the precautionary measures must be most strictly observed (see Sutton's "Vol. Anal.," p. 299).

Uses.—The pure metal is used in volumetric analysis for standardising sodium chloride solutions. According to Stein,

chips of the finest lace-silver are used instead of metallic copper for reducing the oxides of nitrogen in ultimate organic analysis. Stas recommends reducing the metal from an ammoniacal solution with ammonium sulphite, in order to obtain an absolutely pure silver. This tedious, but accurate, method is described in Post, "Chem.-techn. Analyse," 2nd ed., vol. i., p. 566.

Silver refineries prepare the above-described chemically pure 100 per cent. metal in sheets, as well as the grain silver. The former is well adapted as a standard for sodium chloride solutions. Regarding this method, see Fresenius, "Quant. Anal.," vol. i., p. 237.

Commercial Varieties.—The chemically pure metal is prepared by reduction of the chloride. The so-called grain silver of the refineries, precipitated by means of copper, is never absolutely pure, according to Fresenius ("Quant. Anal.," vol. i., p. 106), and generally contains about $\frac{1}{1000}$ part of copper.

SILVER NITRATE.—Argentum nitric. pur. ($AgNO_3$). Mol. wt., 169·89. Colourless rhombic crystals, or small sticks. Soluble in water (2 : 1). The concentrated aqueous solution must be clear and neutral.

Tests for Impurities.—*Silver Chloride and Saltpetre.*—0·5 gm. is dissolved in an equal quantity of water, 20 c.c. of absolute alcohol added; after shaking for a few minutes the solution must remain clear.

General Impurities.—2 gms. are dissolved in about 60 c.c. of water; the solution is then heated to 70°, and gradually precipitated with the quantity of hydrochloric acid necessary. When the precipitate has settled it is filtered hot, washed, and the filtrate evaporated to dryness and slightly ignited; only traces of residue must remain.

Note.—When an accurate determination is required, a larger quantity of the salt must be taken.

During a discussion regarding the best method of analysing the salt, Mr. H. Rossler, director of the "Deutsche Gold und Silber Scheideanstalt," Frankfort-on-the-Main, informed the author that he employed 100 gms. for the test for impurities, precipitating with hydrochloric acid. After obtaining a highly-concentrated solution by evaporating the filtrate in a porcelain basin, he again diluted with water, heated, filtered, and evaporated to dryness, and after

slight ignition weighed the residue. At the same time, he performed a blank test, evaporating the same quantity of water, 100 c.c. of the purest nitric acid (1 : 20), and 50 c.c. hydrochloric acid (1 : 19) in a porcelain basin, and subtracting the residue obtained from the above. The author has found good samples to leave from 0·01 to 0·03 per cent. of residue when tested by this very accurate method. Such small traces consisting generally of calcium nitrate, with minute traces of copper and iron, cannot be avoided during the manufacture, and are of no importance in the use of the salt for silver nitrate solutions.

Quantitative Estimation.—See under "Silver," p. 282.

Uses, Storage, and Deci-normal Silver Nitrate.—The salt is used for the detection, separation and estimation of the halogens, and also for the identification of chromic, arsenious and formic acids. Ammoniacal silver nitrate solution and silver oxide are frequently used in the investigation of organic substances, and for the detection of the aldehydes, in presence of which an ammoniacal solution of silver is reduced with formation of a mirror.

Deci-normal Silver Nitrate.—This is the solution generally employed, and may be prepared by dissolving 16·989 gms. of the purest salt in a litre of water. The salt, pure for analysis, should be used, but as the metal itself can be obtained in a high state of purity, the solution is often made by dissolving 10·788 gms. in nitric acid, evaporating, and diluting the residue to 1 litre. Standard solutions of silver salts ought to be kept in brown bottles. Barille ("Rép. de Pharm.," 1891, 47, p. 403) prefers to mix ground pumice stone or glass beads with the silver nitrate sticks instead of linseed for keeping purposes, as the use of the latter occasions a loss of silver through the action of the oil contained in the seeds.

Commercial Varieties.—The following varieties are in the market: (1) silver nitrate, from potassium nitrate; (2) silver nitrate, from silver chloride; and (3) silver nitrate, from lead nitrate, the first of these being used for medicinal purposes. These preparations cannot be mistaken for the salt under consideration if the tests for saltpetre, silver chloride and lead are applied.

SILVER NITRITE.—Argentum nitrosum. puriss. ($AgNO_2$).

Mol. wt., 153·89. Yellowish needles or prisms, difficultly soluble in water.

The salt is prepared by precipitation from a concentrated solution of potassium nitrite by means of silver nitrate, with recrystallisation of the product. It is used for standardising permanganate solution for the estimation of nitrites, and must contain from 99·5 to 100 per cent. pure salt. Its estimation may be conducted as under "Potassium Nitrite," p. 250. See particularly footnote, p, 266.

SODA LIME.—Preparation.—Take 100 gms. of sodium hydrate, dissolve in 500 c.c. of water. Add to the solution 200 gms. of good white freshly-burnt lime. Allow it to slake, then evaporate the whole to dryness, stirring from time to time to prevent the whole solidifying into a mass. Break up the mass and place it in an iron crucible. Heat to a low red and allow to cool, but while still warm break it up into small pieces in an iron mortar. Pass the whole through a sieve of wire gauze $\frac{1}{8}$ in. mesh, then again sieve the finer portion through a sieve with $\frac{1}{12}$ in. mesh. Keep the granular portion and the powder in separate bottles with waxed corks. The coarser portion may be again powdered until it passes through the coarser sieve.

Tests for Purity.—On addition of hydrochloric acid there should be little or no effervescence.

A blank combustion should be performed with pure sugar, to ensure that it does not yield any ammonia.

Uses.—Is employed in the estimation of nitrogen in organic compounds, also for the absorption of carbonic acid.

SODIO-AMMONIUM PHOSPHATE.—Natrium phosphoric. ammoniat. pur.: microcosmic salt ($PO_4HNa(NH_4)4H_2O$). Mol. wt., 209·15. Colourless monoclinic crystals, showing a clear, colourless bead when fused on platinum wire; soluble in water to a clear solution, with slightly alkaline reaction.

Tests for Impurities.—As under "Sodium Phosphate".

Quantitative Estimation.—The phosphoric acid is estimated as under "Sodium Phosphate," and the ammonia as under "Ammonium Chloride".

Uses.—The salt is an important blowpipe reagent, and is

also used for standardising uranium solution (see "Sodium Phosphate," "Uses").

Commercial Varieties.—These are liable to contain the same impurities as sodium phosphate.

SODIUM.—Natrium metallic (Na). At. wt., 23. Silvery white metal, of the consistency of beeswax at the ordinary temperature.

Tests for Impurities.—*Foreign Metals.*—The sodium hydrate obtained by acting upon the metal with water must give no reaction with ammonium sulphide, and on acidifying a similarly prepared solution with hydrochloric acid and passing hydrogen sulphide no precipitate must appear.

Note.—On dissolving commercial sodium in water a turbid solution, due to impurities, is often obtained, but when the metal is to be used as a reducing agent these are of no importance. Sulphur or arsenic is seldom found; however, they may be tested for in the hydrogen evolved after treatment with water, by means of lead and silver paper (see "Aluminium"). The presence of nitrogen can be detected by the smell of ammonia on heating the caustic soda solution.

Quantitative Estimation.—The metal is dissolved in water, and the solution titrated; a suitable apparatus for effecting solution without loss is described below under "Uses".

Uses and Storage.—Sodium is often used in analysis for the production of nascent hydrogen, and, among other uses, for the detection of nitric and sulphurous acids and arsenic. It is generally used for such purposes in the form of sodium-amalgam, a grey, dry substance containing about 2 per cent. of sodium, and giving a quiet, regular evolution of gas. Sodium may also be used for establishing the strength of standard acid solutions ("Zeit. f. anal. Chem.," 1893, p. 422). Rosenfeld ("Zeit. f. prakt. Chem.," 1893, p. 599, and "J.S.C.I.," 1894, p. 249) passes a slow current of steam over the metal, and conveys the hydrogen formed into distilled water by means of a short glass tube attached to india-rubber tubing in order to avoid loss. The water retains any caustic soda which may have passed over, and using 23 gms. of sodium he obtained an exactly normal solution. Details regarding this apparatus are described in the above-mentioned paper.

Sodium is generally preserved in paraffin oil, but this

method has given rise to explosions, an instance being recorded ("Chem. News," vol. lxv., p. 75) of the explosion of a bottle containing 0·9 kilogram preserved in this way. No reason could be ascribed for the occurrence, but Phipson, the observer, conjectured that the paraffin oil might have been moist, or had been purified with sulphuric acid, and the latter imperfectly removed. There is also a possibility of a prolonged deoxidising action of sodium on an impure oxidised oil giving rise to the formation of water or an organic acid. In consequence of this danger, W. Vaubel ("J.S.C.I.," 1892, p. 753) recommends vaseline oil, under which it has been known to keep well for years, wiping the metal with dry filter paper being quite sufficient to remove all traces of oil. Both the so-called "safety oil" and a petroleum product are said to be very well adapted for this purpose ("Chem.-Ztg.," 19, pp. 1682-3).

Commercial Varieties.—Sodium is sold in sticks, lumps, or cubes, it is also formed into wire for dehydrating ether, etc.

SODIUM ACETATE.—Natrium aceticum, puriss.: acetate of sodium ($C_2H_3O_2Na$, $3H_2O$). Mol. wt., 136·08. Colourless, transparent rhombic crystals, efflorescing in a warm atmosphere and forming a slightly alkaline solution with 1 part of water; soluble in 23 parts cold and 1 part boiling alcohol.

Note.—On the reactions of sodium acetate, see "J.S.C.I.," 1893, p. 467.

Tests for Impurities.—*Solubility.*—See above.

Metals, Sulphuric Acid, Chlorine, and Iron.—The aqueous solution (1 : 20) must give no reaction with either hydrogen sulphide, barium nitrate, or ammonium oxalate. On adding an equal quantity of water, acidifying with nitric acid, and adding silver nitrate, no precipitate must appear, and 20 c.c. of the same aqueous solution must show no reaction with 0·5 c.c. of potassium ferrocyanide solution.

Quantitative Estimation.—The best and most accurate determination of the acetic acid in acetates is by Fresenius's method—namely, distillation with phosphoric acid and titration of the distillate; and G. Neumann ("Zeit. f. angew. Chem.," 1889, p. 24, and "J.S.C.I.," 1888, p. 645) describes an apparatus for conducting this estimation. Harcourt Phillips ("Chem.

News," 1886, p. 181) finds this method a very accurate one and better suited for the analysis of acetate of lime than the so-called "Glauber salt method". According to this method, the acetate of lime is first converted into sodium acetate by adding sodium sulphate, this is converted by ignition into sodium carbonate, which is then dissolved in water and titrated.

As acetates are largely used for technical purposes, many simple methods have been proposed for use in factories, such as the direct titration method of A. Sonnenschein, which is based on the fact that methylaniline orange (Orange IV.) is not affected by acetic acid, but is coloured red by mineral acids ("J.S.C.I.," 1887, p. 563).

Uses.—Acetate of soda is used for the precipitation of iron and alumina, and also in the titration of phosphoric acid by the uranium method; further, as an important quantitative test for narcotine, papaverine, and narceine. It is also used for the quantitative estimation and separation of the more important alkaloids of opium (Plugge, "Analyst," 1887, p. 197).

Commercial Varieties.—The so-called "red salt," generally fairly pure, and the raw acetate may be obtained; the latter often contains carbon and soda. Sonnenschein (loc. cit.) found 91 and 95 per cent. sodium acetate in two samples respectively.

SODIUM BICARBONATE.—Natrium bicarbonic. puriss. ($NaHCO_3$). Mol. wt., 84·01. White crystalline (monoclinic) crusts, or powder, of slightly alkaline taste, and giving a clear solution with water (1 : 12). The flame, when seen through an indigo prism or cobalt glass, must not appear violet, or, if so, only momentarily.

Tests for Impurities.—*Heavy Metals, Silicic, Sulphuric, and Phosphoric Acids.*—These tests, using a gram or two of the salt, are performed as under "Sodium Carbonate".

Ammonia.—On heating in a test tube, no smell of ammonia must be detected, and moist turmeric paper must not be coloured brown by the vapours evolved.

Chlorine, Thiosulphate, Arsenic.—The aqueous solution (1 : 50) acidified with acetic acid must show only a slight opalescence with silver nitrate.

Monocarbonate.—A solution of 1 gm. in 20 c.c. of water (obtained without agitating the liquid, and at a temperature not exceeding 15°) must not at once assume a red colour on the addition of 3 drops of phenolphthalein; should, however, a slight reddish colour be visible it ought to disappear on adding 0·2 c.c. normal hydrochloric acid.

Potash Salt.—See "Note".

Note.—Numerous investigations have recently been made on the bicarbonate, of which a full and detailed account has been published by the Society of German Pharmaceutical Chemists. The most important points in this report are given here as follows: Salts of sodium may be tested for potassium by the flame, the colour being observed through blue glass, when a violet colour must not appear for any length of time. This test is fairly delicate, as a fraction of a per cent. of potassium imparts a continuous violet colour to the flame. Regarding the test for ammonia (i.e., heating the dry salt in a test tube), 1 per cent. may be distinctly detected by smell, and even 0·02 per cent. when moistened turmeric paper is fixed to the upper part of the tube.

Chlorine, Thiosulphate, Arsenic.—On testing the solution as already described, a whitish turbidity shows presence of chlorine, a reddish or yellowish turbidity, arsenic, and a brown or blackish turbidity thiosulphate. If, therefore, after the lapse of a few minutes only a slight whitish opalescence is noticeable, it may safely be inferred that neither arsenic nor thiosulphate are present in any appreciable quantity. Arsenic may also be easily found by Marsh's test; also if, on dissolving the salt in dilute sulphuric acid and adding metallic zinc, no hydrogen sulphide is detected on testing with lead acetate paper, there is no thiosulphate present. The cold solution of the salt, in absence of monocarbonate, may also be tested for thiosulphate with iodine solution, the colour of which must not be immediately discharged (see Salzer, "J.C.S.," 1887, A., p. 79).

Monocarbonate.—According to the investigations of the Pharmaceutical Commission, Kremel's phenolphthalein test (see above), if carefully performed, is very satisfactory, but the reaction must be noted at once. If the salt contains less than 2 per cent. monocarbonate, 3 drops of phenolphthalein produce no coloration. A little of this impurity is found in nearly every sample, and the salt must be carefully dissolved, as loss of carbonic acid ensues, even at the ordinary temperature, particularly on shaking. This test is superior to the old method with mercuric chloride, but in presence of ammonia salts the phenolphthalein test is also unreliable.

Quantitative Estimation.—This is performed in order to estimate the monocarbonate present, and if the sample is free

from chlorides and sulphates, and has been dried over sulphuric acid, the monocarbonate may be found by simple titration with acid. As an example, if 5 gms. of the pure salt are dissolved in 62 c.c. normal acid, 25 c.c. $\frac{n}{10}$ alkali are necessary for neutralisation; if the sample contains 1 per cent. monocarbonate, only 21·4 c.c. will be required, if 2 per cent. 17·9 c.c., and 3 per cent. 14·4 c.c. In order to execute an accurate analysis of a sample containing moisture, chlorides, and sulphates, the Na_2O is estimated alkalimetrically, as in sodium carbonate, and the CO_2 gravimetrically, or volumetrically. Fresenius, in his "Quantitative Analysis," describes an apparatus for a convenient gravimetric estimation of CO_2. From the amount of Na_2O and CO_2 found, the percentage of mono- and bicarbonate may easily be calculated.

Note.—In making this calculation it is necessary first of all to find how much of the CO_2 is used by the Na_2O to form monocarbonate, and what quantity of the latter is thus formed; secondly, the quantity of CO_2 left; and thirdly, how much of the monocarbonate calculated above can be converted into bicarbonate from the CO_2 left; this should give the amount of bicarbonate present. On now subtracting the amount of Na_2CO_3 equivalent to the bicarbonate found from the Na_2CO_3 calculated at first, the amount of monocarbonate present is found.

Example.—1 gm. of sodium bicarbonate contains 0·37 gm. Na_2O and 0·52 gm. CO_2, and, according to the equation $Na_2O + CO_2 = Na_2CO_3$, the 0·37 gm. Na_2O will require 0·2626 gm. CO_2 for conversion into monocarbonate, the amount formed being 0·6326 gm. On subtracting the 0·2626 gm. CO_2 from the total CO_2 (0·52 gm.), 0·2574 gm. remains, and from the equation $Na_2CO_3 + CO_2 + H_2O = 2(NaHCO_3)$ this quantity is capable of converting 0·6200 gm. monocarbonate into bicarbonate, forming 0·9827 gm. bicarbonate. As 1 gm. of the sample was taken, the percentage is 98·27. The monocarbonate may be calculated as follows: The amount of Na_2CO_3 equivalent to the $NaHCO_3$ found is 0·6200 gm., and this subtracted from 0·6326 gives 0·0126 gm., or 1·26 per cent. monocarbonate. The sample, therefore, consists of 98·27 per cent. $NaHCO_3$ and 1·26 per cent. Na_2CO_3, the difference of 0·47 per cent. representing moisture, etc. A sample on analysis gave 37·21 per cent. Na_2O and 48·67 per cent. CO_2, and consisted, therefore, of 85 per cent. $NaHCO_3$, 10 per cent. Na_2CO_3, and 5 per cent. moisture, etc.

R. Reith has devised a volumetric method for the estimation of the CO_2 and alkali in sodium bicarbonate ("Volumetrische

Analyse," 1883, p. 101). Lunge has also published a method for the estimation of alkaline monocarbonate in presence of bicarbonate; the process finds general use in alkali manufacture, and is well adapted for the analysis of the salt under consideration (see Lunge's "Alkali and Sulphuric Acid"; also Sutton, "Vol. Anal.," p. 58; also "Zeit. f. angew. Chem.," 1897, vol. vi., p. 169).

Uses and Storage.—The pure salt is used as a neutralising agent, and in forensic analysis for the detection of alkaloids in place of the normal carbonate. Mohr considers the salt to be well adapted for the preparation of dehydrated sodium carbonate for standard solutions, the conversion being effected by ignition. It is worthy of note that, according to Kissling ("J.C.S.," 1891, A., p. 364), sodium carbonate loses traces of CO_2 on ignition, with formation of free alkali; the carbonate will therefore always give a slight reaction with Dobbin's reagent (see p. 299). Dehydrated carbonate prepared from bicarbonate, and its employment as a standard for the titration of acids, are referred to under "Sodium Carbonate". The salt must be kept in well-stoppered bottles.

Commercial Varieties.—Even in very pure preparations, minute traces of chlorine, sulphuric, acid and monocarbonate are always present, and commercially pure samples contain distinct traces of the two former impurities, in addition to a few per cent. monocarbonate. Lehmann ("Pharm. Ztg.," 1888, p. 42) found in a sample labelled "Natr. bic. pur. germ." 2·6 per cent. ammonium carbonate and 0·06 per cent. sodium thiosulphate. Less pure varieties, some of which are obtained by the ammonia process, and especially of English manufacture, have been often found to contain considerable quantities of common salt, ammonium chloride or carbonate, and also thiosulphate ("Rep. d. Chem.-Ztg.," 1887, p. 288; "Arch. d. Pharm.," 1888, p. 35; "Pharm. Ztg.," 1889, p. 198). Some years ago Mylius and Wimmel detected thiosulphate and arsenic. The presence of ammonia in the cheaper qualities was pointed out some time ago, and the author has detected this impurity and thiosulphate in similar samples,[1] and has

[1] For the quantitative estimation of ammonia, the salt is boiled with caustic soda solution; the ammonia evolved retained by standard hydrochloric acid, and the solution titrated with standard alkali.

had to reject them. The better qualities are generally very pure, containing very small traces of the impurities already referred to here, and such samples stand the test required by the German Pharmacopœia, and even far more stringent tests.

SODIUM BICHROMATE.—Natrium bichromicum, puriss. ($Na_2Cr_2O_7$, $2H_2O$). Mol. wt., 298·03. Red, hygroscopic crystals.

Tests for Impurities.—As under "Potassium Bichromate".

Quantitative Estimation.—The method is the same as for the potassium salt; or the solution may be titrated with ferrous ammonium sulphate, using potassium ferricyanide as indicator, a drop of the solution being brought in contact from time to time with a drop of ferricyanide. The iron solution is standardised on chemically pure potassium bichromate, and may be checked with permanganate solution which has been previously standardised on potassium tetroxalate (see "Chem.-Ztg.," 1891, p. 373). For the testing of chromates by Zulkowski's method, which is a satisfactory one, see Liebig's "Annalen," 1891, p. 357 *et seq.*

Uses and Storage.—The salt is employed as an oxidising agent, and must be well protected during storage.

Commercial Varieties.—For technical purposes the salt is sold either in the crystalline or fused state, the latter containing very little water. R. Kissling ("J.S.C.I.," 1891, p. 461) gives the following analyses of commercial samples:—

(*a*) English manufacture, containing 10 to 13 per cent. of water and 83·79 to 88·42 per cent. of the pure salt.

(*b*) German manufacture, containing 11 to 12 per cent. and 87·90 to 88·39 per cent.

(*c*) German manufacture containing 6·6 per cent. and 92·84 per cent.

(*d*) German, fused, containing 7·1 per cent. and 88·61 per cent. The dehydrated salt is generally sold with a guarantee of about 74 per cent. chromic acid.

SODIUM BISULPHATE.—Natrium bisulphuricum, puriss.: acid sulphate of soda ($NaHSO_4$, H_2O). Mol. wt., 138·08. Colourless triclinic crystals. The salt must give a clear,

colourless solution with water and show a strong acid reaction. As a rule the salt crystallises with 1 molecule of water.

Tests for Impurities.—As under "Potassium Bisulphate".

Test for potassium, see "Sodium Bicarbonate".

Quantitative Estimation.—A weighed quantity is dissolved in water, the sulphuric acid precipitated with barium chloride, and the barium sulphate weighed. To the filtrate sulphuric acid is added in excess; the solution is then filtered, evaporated, and the residue finally ignited with ammonium carbonate until excess of sulphuric acid is removed. The sodium sulphate left is then weighed. If the residue has to be tested for potash, the sulphate must be converted into chloride by means of barium chloride, and platinic chloride added to the concentrated solution. In most cases it will be sufficient to estimate the sulphuric acid by the method described above, or the solution may be titrated with normal alkali solution, using litmus as indicator. 1 c.c. equal 0·12068 gm. $NaHSO_4$.

Uses and Storage.—The salt is used as a fusion agent for minerals difficult to decompose, and the usual precautions must be adopted in storage.

Commercial Varieties.—The pure salt is sold either in the crystalline state or fused. The author has often come across samples having the wrong composition owing to their containing too little sulphuric acid. A crude bisulphate, generally containing arsenic and iron, can also be obtained.

SODIUM BISULPHITE.—Natrium bisulphurosum, pur.: acid sulphite of soda ($NaHSO_3$). Mol. wt., 104·07. White powder, with a strong smell of SO_2. The aqueous solution shows an acid reaction. The salt should contain from 90 to 95 per cent. $NaHSO_3$.

Tests for Impurities.—*Arsenic.*—5 gms. are evaporated to dryness with pure concentrated sulphuric acid; on dissolving the residue and passing hydrogen sulphide no reaction must take place, and on addition of nitric acid solution of ammonium molybdate no yellow colour must appear on heating slightly.

Quantitative Estimation.—According to the iodine method of Bunsen, 5 gms. are dissolved in a litre of freshly boiled and cooled distilled water, the cooling being conducted in a closed

vessel. A portion of the solution is then measured off with a pipette and diluted with the boiled water until 100 c.c. contain a maximum of 0·04 gm. SO_2; in other words, the solution must not use more than about 12 c.c. $\frac{n}{10}$ iodine. A solution of starch is now added, and the solution titrated with $\frac{n}{10}$ iodine until a blue colour appears. 1 c.c. $\frac{n}{10}$ iodine equals 0·003203 gm. SO_2. The sulphites may also be estimated alkalimetrically, using methyl orange as indicator, according to Lunge. Litmus and phenacetolin are not well adapted for this purpose. The method is described in Sutton. Ch. Blarez ("J.C.S.," 1886, A., p. 918) has published an article on the behaviour of sulphurous acid towards various indicators, and its estimation by standard acid in presence of other acids.

Uses and Storage.—The salt is a strong reducing agent, and is used particularly for the conversion of arsenic into arsenious acid, chromic acid into oxide, and the reduction of ferric oxide; it is also used for other purposes in analysis. It must be kept in well-stoppered bottles.

Commercial Varieties.—Sodium bisulphite, dry, for technical purposes, the pure dry salt, and the preparation for analytical purposes, which latter must be free from arsenic in particular, may all be obtained. On drying the salt in the atmosphere a slight loss of SO_2 always ensues, which excludes the possibility of preparing a commercial salt containing 100 per cent., or of even giving an accurate guarantee of its percentage. Good preparations should have the above-mentioned percentage, but the salt deteriorates during storage, and particularly in contact with air; this also applies to the aqueous solution, the sulphate being slowly formed.

Sodium Sulphite (Na_2SO_3 + aq.) must answer the same tests, and serves the same purpose as the above.

SODIUM BORATE.—Natrium biboracicum, pur.: borax ($Na_2B_4O_7$, $10H_2O$). Mol. wt., 382·16. Hard, white monoclinic crystals, soluble in 17 parts of cold, and 0·5 part of boiling water. The aqueous solution must be clear, give an alkaline reaction, and, after slightly acidifying with hydrochloric acid, must impart a red colour to turmeric paper.

Tests for Impurities.—*Metals, Earths.*—The hot aqueous

solution (1 : 30), after acidifying with hydrochloric acid, must give no reaction with hydrogen sulphide water, and, on adding excess of sodium carbonate to the same solution, no precipitate must form.

Carbonates, Sulphates, and Chlorides.—On acidifying the aqueous solution (1 : 30) with nitric acid, no carbonic acid must be evolved, and subsequent addition of barium and silver nitrates must not produce any change.

Water.—The salt, after grinding to fine powder and drying by exposure to the air, must lose 47·1 per cent. on ignition.

Note.—The ordinary prismatic borax, with 10 molecules of water, shows the above loss on ignition, but the octahedral modification, crystallised at a temperature over 60°, or from supersaturated solution, contains only 5 molecules of water of crystallisation. As the former is employed for standardising acid solutions it is necessary to estimate the water present before use, as the sample may contain crystals of the octahedral form; as an alternative, the borax may be estimated by normal acid, 5·24 c.c. of which correspond to 1 gm. borax (see Rimbach, "J.S.C I.," 1893, p. 466; also Salzer, "J S.C.I.," 1894, p. 280).

Quantitative Estimation.—In the absence of free alkali or carbonate, commercial samples may be tested by titration. When exactly sufficient sulphuric acid has been added to set free the boracic acid, litmus indicator assumes a claret colour,[1] changing instantly to a lighter red in presence of the slightest excess of sulphuric acid. One molecule of borax (382) requires 1 molecule sulphuric acid (98) for decomposition. On the employment of methyl orange as indicator in this method, see Sutton, "Vol. Anal.," 7th ed., p. 92. By Rosenbladt's method the boric acid is converted into boric methyl ester, which is separated by distillation, and, after decomposing the ester by lime water, the boric acid is weighed as calcium borate. The titration method is the best, however, the above being more useful for determining small amounts. Borax may also be estimated by neutralising with sulphuric acid in presence of methyl orange, then adding glycerin and titrating with soda in presence of phenolphthalein (see Sutton, loc. cit.).

Uses.—Borax plays an important part in blowpipe analysis,

[1] C. Schwarz titrates with hydrochloric acid, using congo red as indicator ("J.S.C.I.," 1888, p. 45).

and for that purpose must be dehydrated by gentle ignition in a platinum capsule till the intumescence subsides (calcined borax); in this condition it is also used in metallurgy. Salzer recommends the use of pure borax as a standard in alkalimetry and acidimetry. Salzer and Rimbach employ a decinormal borax solution, which keeps very well.

Commercial Varieties.—The pharmaceutical preparation (refined borax) is the prismatic form, and the hard, octahedral borax finds use for technical purposes. Calcined borax and borax glass are also used in analytical work, and are both free from water, but take up moisture from the atmosphere, the glass becoming opaque. Refined borax is generally pure, as its appearance shows. English borax has been said to contain as much as 20 per cent. of sodium phosphate (Böckmann), but the author has never found this impurity, which might readily be detected by ammonium molybdate.

SODIUM BROMATE.—Natrium bromicum, puriss. ($NaBrO_3$). Mol. wt., 150·92. Crystals, easily soluble in water, solution in which must be clear.

Tests for Impurities.—As under "Potassium Bromate," p. 239.

SODIUM CARBONATE (PURE CRYSTALLISED).—Natrium carbonic. cryst. chem. pur.: carbonate of soda (Na_2CO_3, $10H_2O$). Mol. wt., 286·16. Large, colourless, transparent monoclinic crystals. Soluble in water (Na_2CO_3 1 : 7).

Tests for Impurities.—*Solubility.*—20 gms. must give a clear, colourless solution with 80 c.c. of water.

Silicic Acid.—On evaporating 20 gms. with excess of dilute hydrochloric acid, drying the residue for some time at 100° C., moistening with strong acid and about 150 c.c. of water, the solution must be clear and show no scales of silicic acid.

Sulphuric Acid.—On dissolving 10 gms. in 150 c.c. of water, acidifying slightly with hydrochloric acid, heating to boiling, and adding barium chloride, no precipitate must form after 12 hours' standing.

Chlorides.—A solution of 5 gms. in 50 c.c. of water, slightly

acidified with nitric acid, must give no reaction with silver nitrate.

Arsenic.—10 gms. of granulated zinc, free from arsenic, are placed in a Marsh apparatus of about 200 c.c. capacity and dilute sulphuric acid (1 : 3) added, and the test for arsenic applied in the usual way. 30 gms. of the carbonate are dissolved in a little water, the solution acidified with the dilute acid, and transferred to the apparatus, which is kept going for half an hour, during which time no arsenic mirror must have appeared.

Note.—Fresenius and Otto both record having detected arsenic in carbonate of soda, and they separately call attention to the necessity of testing for this impurity when the carbonate has to be employed for forensic work (Otto, "Ausmittelung der Gifte," 6th ed., p. 149).

Heavy Metals, Lime, etc.—20 gms. are dissolved in 60 c.c. of water, acidified with hydrochloric acid, and hydrogen sulphide water added. No change must take place, and on adding ammonia, ammonium sulphide, and ammonium oxalate, the solution must not show a precipitate or turbidity, nor be greenish in colour. For potassium sulphocyanide test, see under "Uses".

Phosphoric Acid.—The test is performed as under "Potassium Hydrate," using 20 gms. of the sample.

Thiosulphate, Ammonia, Potassium.—See note under "Sodium Bicarbonate," p. 288. Sodium carbonate must be free from ammonia.

Alkaline Hydrate is tested for by Dobbin's reagent (see note, p. 299).

Sodium Bicarbonate.—A quantitative estimation is performed by the method recommended in Böckmann, "Chem.-techn. Unters.," 3rd ed., vol. i., p. 390, for testing soda ash made by the ammonia process. Its presence may also be detected by heating the effloresced salt to about 150° and passing the carbonic acid evolved (if bicarbonate is present) into baryta water. For use as a precipitant or as a flux the presence of bicarbonate is not objectionable, and the absence of bicarbonate is only essential in the case of the hydrated form used as a standard, which must not evolve any CO_2 on careful ignition.

Quantitative Estimation.—A solution of 5 gms. in 50 c.c.

of water is heated to boiling, litmus added, and the boiling solution titrated with normal hydrochloric acid until the red colour remains permanent. 1 c.c. normal acid equals 0·053 gm. Na_2CO_3, or 0·1430 gm. Na_2CO_3, $10H_2O$. In alkali manufacture, methyl orange is used as indicator, the sulphuric acid used for titration being standardised on pure sodium carbonate, and is so prepared that 50 c.c. will exactly neutralise 5 gms. Na_2CO_3. Reinitzer ("Zeit. f. angew. Chem.," 1894, p. 447 *et seq.*) records an accurate method of performing a complete volumetric analysis of the carbonate. The titration of the alkaline carbonates and their analysis are also described in Sutton. Lunge ("Analyst," 1895, p. 65) recommends certain precautions to be taken in employing methyl orange as an indicator. A quantitative analysis is only made as a general rule when the anhydrous salt is being examined, as the external appearance and qualitative examination of the crystallised salt is a good enough guide as to its purity.

Uses and Storage.—The crystallised salt is used as a precipitating and neutralising agent, and for the decomposition of a number of insoluble salts containing an alkaline earth or metal as base, particularly when in combination with an organic acid. The salt should be stored in glass bottles. Richards ("Chem. News," 1892, p. 245) gives a method for preparing an absolutely pure sodium carbonate, which he used in determining the atomic weight of copper. This preparation showed no colour with ammonium sulphide, either before or after neutralisation, no reaction with potassium sulphocyanide, and contained neither chlorides nor sulphates. It was pure white in colour, gave a perfectly clear, colourless solution with water, and the solution emitted no odour on heating. The only impurities present consisted of infinitesimal traces of silicic acid and alumina, which, as Stas affirms, cannot be got rid of entirely, even when using the greatest precaution.

Commercial Varieties.—For special analytical work it is necessary to use the chemically pure preparation, but for general use the puriss. is sufficiently good. This latter contains slight traces of iron, chlorides, and sulphates.

SODIUM CARBONATE (PURE ANHYDROUS).—Natrium carb. sicc. chem. pur. (Na_2CO_3). A white, dry powder.

Tests for Impurities.—The same tests as the preceding are applied, but as the salt is dehydrated, only one-third the quantities given should be used. The various qualities of this preparation are detailed under "Commercial Varieties".

Note.—The dehydration must be carefully conducted, as at a higher temperature than that necessary a loss of CO_2 takes place, and in this way traces of caustic alkali may be formed. These may be detected by Dobbin's reagent — ammoniacal potassio-mercuric iodide. According to Kissling ("Rep. d. Chem.-Ztg.," 1890, p. 136) this reagent may be prepared as follows: A solution of about 5 gms. potassium iodide is mixed with a solution of mercuric chloride till the precipitate formed just ceases to redissolve. The solution is then filtered off, and 1 gm. of ammonium chloride added; a dilute solution of caustic soda is carefully introduced until a slight permanent precipitate forms. The solution is now finally filtered and made up to a litre. The best method of detecting alkaline hydrate is to place the substance under examination on a watch-glass and pour some of the solution over it; the slightest trace will be at once evidenced by the appearance of a yellow colour (see also paper by L. Dobbin, "J.S.C I.," 1888, p. 829).

Quantitative Estimation.—See under "Uses".

Uses and Storage.—It is used as a blowpipe reagent, and a mixture of the chemically pure anhydrous carbonates of potassium and sodium is employed as a flux for silicates. In forensic chemical analysis the pure carbonate is often used in the investigation of alkaloids and metallic poisons. As before mentioned, the absolutely anhydrous salt is used as a standard in acidimetry, and is obtained by igniting to a dull red heat chemically pure bicarbonate of soda. The best method of checking the carbonate is by titration with normal hydrochloric acid, previously standardised on Iceland spar. The anhydrous carbonate absorbs moisture from the atmosphere up to about 10 per cent. in course of time, and must therefore be kept well sealed.

Commercial Varieties.—The following kinds are prepared:—

(*a*) Chemically pure dry sodium carbonate in powder, containing about 1 molecule of water. Regarding this preparation, Kissling ("Chem.-Ztg.," 1890, p. 136) considers the carbonate, pure for analysis, sold by E. Merck, to be the purest of all those he tested; this salt consists only of sodium,

carbonic acid and water, and loses 0·63 per cent. CO_2 and 14·76 per cent. of water at 150°, containing, therefore, a little bicarbonate.

(*b*) Chemically pure anhydrous carbonate; also perfectly pure, but may contain 2 or 3 per cent. of water, and sometimes a little bicarbonate.

(*c*) Chemically pure carbonate, used as a standard for acids. This must also be perfectly pure, free from water and bicarbonate, and must contain 100 per cent. For its analysis, see "Uses".

SODIUM CARBONATE, CRUDE.—Natrium carb. crudum: soda ash (Na_2CO_3) and soda crystals ($Na_2CO_3 10H_2O$). It may be obtained either calcined or in crystals. Soda crystals dissolve more readily, contain less ferric oxide, and are free from hydrate and insoluble matter. They contain up to 65 per cent. of water and several per cent. of sulphates, chlorides, etc. The German Pharmacopœia demands at least 32 per cent. Na_2CO_3. Soda ash may now be purchased with a guaranteed percentage of, in many cases, 98 to 99 per cent. The product obtained by the ammonia-soda process has, in particular, attained a high degree of purity of late, and there has been also a marked improvement in that by the Leblanc method. Böckmann considers that a good sample ought to answer the following specification: There must not be present more than 0·5 per cent. of water, 0·1 insoluble in hydrochloric acid, and 0·02 ferric oxide. Ammonia-soda (calcined soda), particularly Solvay-soda, contains considerably less than these maxima. It contains less than 0·1 per cent. of sulphate, and good Leblanc soda ash contains from 0·5 to 1 per cent. The proportionate amount of sodium chloride present in the ammonia product is 0·5 per cent. with a 98 per cent., and 2·5 per cent. with a 96 per cent. sample, and good Leblanc contains from 0·25 to 0·5 per cent. The strength of soda ash is expressed differently in the various countries; for example, in England we find the available soda calculated to sodium oxide (Na_2O); in Germany it is recorded as carbonate, and in France and Belgium as degrees Descroizilles. A table showing the relation between these methods has been compiled by Pattison,

and brought up to date by Lunge, and is recorded in the various handbooks (e.g. "The Alkali-makers' Handbook," Lunge and Hurter, p. 139 *et seq.*).

In addition to the estimation of the carbonate present, the following tests may be of some importance: Specific gravity, solubility in water, insoluble, etc., percentage of soluble and insoluble iron chlorides, sulphates, sodium thiosulphate, sulphide, silicate, bicarbonate, and hydrate. Lunge's "Manufacture of Alkali and Sulphuric Acid" gives detailed analyses of soda ash. The percentage of water must also be estimated, as the product may have absorbed moisture during storage.

SODIUM CHLORIDE. — Natrium chlorat. chem. pur. (NaCl). Mol. wt., 58·46. White cubic crystals or crystalline powder. Soluble in water (1 : 2·9).

Tests for Impurities. — *Solubility, Sulphuric Acid.*—3 gms. must give a clear, neutral solution, with 20 c.c. of water, and on diluting this solution to 80 c.c., heating to boiling, and adding barium chloride, no precipitate should form even after several hours.

Alkaline Earths, Heavy Metals.—3 gms. are dissolved in 50 c.c. of water, and, after heating to boiling, ammonium oxalate, sodium carbonate and ammonium sulphide added; the solution must not turn turbid.

Iodine.—20 c.c. of the aqueous solution (1 : 20), to which ferric chloride and starch solution have been added, must show no turbidity.

Potassium. — A concentrated solution must show no precipitate with platinum bichloride, even after long standing.

Ammonia.—When heated with caustic soda no smell of ammonia must be detected.

Quantitative Estimation.—A solution is made containing 0·2 gm. in 100 c.c. of water; a few drops of potassium chromate are then added, and the solution titrated with decinormal silver nitrate till a faint red colour appears. 1 c.c. $\frac{n}{10}$ silver nitrate equals 0·005846 gm. NaCl. In the analysis of ordinary common salt, the lime, magnesia, sulphuric acid and water are estimated quantitatively.

Uses and Storage.—The chemically pure salt is used for

standardising silver solutions, and for precipitating the salts of silver. To prepare the decinormal solution the salt is very slightly ignited (not fused, as loss of hydrochloric acid would ensue), and 5·846 gms. weighed out and dissolved in a litre of water ; the solution is tested against decinormal silver nitrate. The salt is also used for producing the sodium flame in polariscope investigations, the dry puriss. salt being taken for this purpose. The usual precautions must be observed in storage.

Commercial Varieties.—These are: the chemically pure salt, the dry puriss., the fused puriss., and ordinary common salt. The first is absolutely pure, and the others of the puriss. class are often sufficiently so for general analytical purposes. The author finds the prevailing impurities in these to consist of slight traces of sulphates, lime or magnesia, and so they do not on this account conform entirely to the above tests. Kubel ("Arch. d. Pharm.," 1888, p. 440) found the commercially pure salt to contain the chlorides of ammonium and magnesium.

SODIUM CHLORIDE, ORDINARY.—Natrium chlorat. crude : common salt.

The Stassfurt rock salt, a well-known German product, contains up to 99 per cent. Hahn found samples containing from 87·39 to 99·45 NaCl ; the KCl ranged from none at all to 0·17 ; $CaCl_2$, 0-0·564 ; $MgCl_2$, 0·07-2·06 ; $CaSO_4$, 0·35-1·334 ; $MgSO_4$, 0-0·485 ; K_2SO_4, 0-0·579 ; Na_2SO_4, 0-1·25 ; $MgCO_3$, 0-0·033 ; in addition to from 0·60-7·91 per cent. of water, and traces of silicic acid and organic substances. According to these figures the sulphates predominate.

J. König ("Chemie der Nahrungsmittel") gives the analyses of various samples (see opposite page).

Bromine, iodine, and lithium are sometimes present in very minute quantities : they occur along with the chlorides of sodium, calcium, and magnesium in the natural salt liquor, but are nearly all retained in the mother liquor during the manufacture. The author found in the mother liquor from Werl works, 3·3754 gms. potassium bromide, 0·0137 gm. potassium iodide, and 8·9833 gms. lithium chloride per litre.

	From Salzungen.			Salzderhelden.	Rodenberg.	Sooden.	Artern.	Sea Salts Analysed by Karsten, St. Ubes.			Rock Salt from Erfurt.
	Ordinary Salt.	Table Salt.	Purest Table Salt.	Ordinary Kitchen Salts.				1.	2.	3.	
	Per Cent.			Per Cent.				Per Cent.			Per Cent.
Moisture	1·96	0·69	0·33	2·26	2·92	3·06	1·20	—	—	—	0·41
Combined water	0·75	0·71	0·72	1·42	1·41	0·90	1·34	2·10	3·10	1·95	0·09
Sodium chloride	97·03	98·16	98·74	95·07	95·27	93·38	95·59	95·86	92·46	96·50	97·83
Potassium chloride	—	—	—	trace	—	—	—	—	—	—	—
Magnesium chloride	—	0·38	0·13	0·22	0·18	0·64	0·46	0·24	0·55	0·32	—
Sodium sulphate	0·46	0·16	0·09	—	0·21	0·94	0·96	—	—	—	—
Calcium sulphate	0·09	—	—	0·27	0·43	0·99	0·51	1·30	2·28	0·88	1·47
Magnesium sulphate	0·03	—	—	0·36	—	—	—	0·35	0·66	0·25	0·24
Insoluble	—	—	—	—	—	—	—	0·15	0·95	0·10	0·25
General appearance	coarse	fine	very fine	coarse	coarse	medium	medium	—	—	—	fine

SODIUM FLUORIDE. — Natrium fluoratum, pur. (NaF). Mol. wt., 42·0. White cubes, soluble in about 25 parts of water.

Tests for Impurities.—See "Hydrofluoric Acid".

Quantitative Estimation.—Hintz and Weber ("J.S.C.I.," 1891, p. 273) describe the correct method to be adopted in making a quantitative estimation of the components of sodium fluoride; they also describe the estimation of silicic acid and fluorine. Sulphuric acid and chlorine they estimate as follows: About 20 gms. of the sample are heated with water, and, after cooling, the liquid is diluted to a litre without filtering, and allowed to settle. (*a*) A measured quantity of the clear solution is transferred to a large platinum capsule, acidified with hydrochloric acid, and barium chloride added. The precipitate is filtered and washed in a platinum funnel, and fused with sodium carbonate, the fused mass is then extracted with water, filtered, acidified again with acid and

reprecipitated with barium chloride. This operation is repeated if necessary. The barium sulphate thus obtained is tested by ignition with sulphuric acid, after which no loss in weight should be observed. (*b*) The chlorine is precipitated in another portion of the clear solution by acidifying with nitric acid and adding silver nitrate; this must also be done in a platinum capsule, and a funnel of the same material must be used for filtering the silver chloride.

Uses and Storage.—The salt is very seldom used in analysis, but is more largely employed for technical purposes. It is kept in india-rubber bottles.

Commercial Varieties.—Hintz and Weber, loc. cit., give the following, as representing the composition of commercial sodium fluoride:—

	Per Cent.
Sodium fluoride	65·65
,, chloride	0·74
,, carbonate	13·89
,, sulphate	1·96
Potassium sulphate	0·74
Soda combined with silicic acid	1·50
Silicic acid partly combined with soda	10·11
Calcium carbonate	0·25
Magnesium carbonate	0·32
Ferric oxide	0·48
Alumina	0·17
Water	3·97
	99·78

The commercial preparation is now purer than formerly, containing up to 97 per cent.

SODIUM HYDRATE.—Natrium hydricum (NaOH). Mol. wt., 40·01.

There are three kinds in use for analytical purposes:—

(*a*) Sodium hydrate, pure from sodium (the purest preparation).

(*b*) Sodium hydrate, pure by alcohol.

(*c*) Sodium hydrate, pure.

1. Sodium Hydrate, pure from Sodium (NaOH + aq.). White crystalline lumps, easily soluble in water and in alcohol.

Tests for Impurities.—The solution in water must be clear, and free from alumina.

Tests as under "Potassium Hydrate, puriss."

Lime and Heavy Metals.—The slightly alkaline solution from the alumina test must give no reaction with ammonium oxalate or ammonium sulphide.

Sulphuric, Nitric, and Silicic Acids.—See "Potassium hydrate".

Chlorine.—A solution (1 : 20) acidified with nitric acid must give no chlorine reaction, or only a very slight opalescence.

Carbonic Acid.—2 gms. are dissolved in 10 c.c. of water, and the solution poured into a mixture of 8 c.c. hydrochloric acid (1 : 12) and 8 c.c. of water; only a few bubbles of gas may appear, but no effervescence. Phosphoric acid must also be tested for as under "Potassium Hydrate," and there must be no ammonia reaction on testing with Nessler's reagent in 1 : 20 solution.

Quantitative Estimation.—The method is the same as that applied to sodium carbonate. If 4 gms. are taken, each c.c. of normal acid is equal to 1 per cent. NaOH. For the estimation of the carbonate present, see "Sodium Hydrate, pure," p. 307.

Uses and Normal Solution.—The uses of the purest sodium hydrate are like those of the potassium preparation.

Normal Caustic Soda.—This solution must contain 40·01 gms. NaOH per litre[1] and, according to Müller, must be practically free from CO_2 for this purpose; the elimination of that impurity may be effected by means of barium hydrate. Methods for preparing the solution and keeping it out of contact with the air are given in various books on the subject. It is generally standardised on normal sulphuric acid, but potassium tetroxalate may also be used.

Commercial Varieties. — When their preparation from metallic sodium has been carefully conducted these always conform to the above tests, and the sodium hydrate, puriss. from sodium, of E. Merck, contains 97 to 99 per cent. NaOH.

[1] See also note under "Normal Alkali Solution," p. 257.

2. Sodium Hydrate, pure by Alcohol ($NaOH + aq.$). White crystalline mass, or thin sticks, giving a clear and colourless solution with water.

Tests for Impurities.—*Solubility, Alumina, Lime, Heavy Metals.*—10 gms. must give a clear solution with 40 c.c. of water, and on diluting to 100 c.c., acidifying with acetic acid, and adding a slight excess of ammonia, only a trace of alumina should be precipitated. The addition of ammonium oxalate and ammonium sulphide must produce no reaction.

Silicic Acid, Chlorides.—As under "Potassium Hydrate, pure by Alcohol".

Nitric Acid.—As under "Potassium Hydrate, puriss."

Sulphuric Acid.—The solution (1 : 20) acidified with hydrochloric acid should only show a slight turbidity on adding barium chloride, so that the solution appears transparent when placed in a test tube of 2 c.m. diameter.

Carbonic Acid.—As under "Sodium Hydrate, pure from Sodium".

Boracic Acid.—See note under "Commercial Varieties".

Quantitative Estimation.—As under "Sodium Hydrate, pure".

Uses.—For the same purposes as potassium hydrate.

Commercial Varieties.—Gerlach found well-crystallised commercial caustic soda to contain 88·96 per cent. Samples are often obtained which contain large quantities of sulphates and chlorides; the author has analysed samples labelled "pure by alcohol" the acidified solutions of which showed strong sulphuric acid and chlorine reactions, and which were no better than the third variety. Venable and Callison ("J.S.C.I.," 1890, p. 968) detected the presence of boric acid, and of several samples obtained from three different factories not one was free from this impurity.[1] According to Hager, the caustic

[1] Samples which were bought as chemically pure, and purified by alcohol or baryta, are said to have contained boric acid, and as the caustic alkalies, particularly caustic potash, are often used for quantitative estimation of this acid, its presence would be distinctly objectionable. It was detected by placing a quantity of the sample in a platinum capsule, adding hydrochloric acid to convert the alkali into chloride, and then moistening the salt with very dilute acid (1 : 100), adding a

alkalies always contain traces of ammonia, absorbed from the atmosphere in the form of carbonate.

3. Sodium Hydrate, pure ($NaOH$ + aq.). White crystalline lumps, or thin sticks, giving a clear and colourless solution with water.

Tests for Impurities.—*Nitric and Carbonic Acids.*—As under "Potassium Hydrate, pure".

Iron, Alumina, Lime.—As under "Sodium Hydrate, pure by Alcohol". Somewhat more alumina is permitted than in the "pure by alcohol".

Quantitative Estimation.—A solution of 20 gms. in 500 c.c. of water is first prepared and the total alkali estimated in 50 c.c., using methyl orange as indicator. To estimate the caustic soda present, 100 c.c. are drawn off, placed in a 250 c.c. flask along with a sufficiency of 10 per cent. barium chloride solution, and the solution made up to the mark with warm water; the flask is then stoppered, shaken, and, after allowing the precipitate to settle, 100 c.c. of the clear solution titrated, using the above indicator. The carbonate of sodium is found from the difference between the total and caustic alkalies. This method is the one generally used; see also "Potassium Hydrate". Gobel ("J.S.C.I.," 1889, p. 726) recommends another method for caustic alkali in presence of carbonate. He adds a drop of phenolphthalein (1 : 20 of alcohol), and titrates the cold solution till colourless, then adds a drop of Poirrier's blue (1 : 400 of water) and continues the titration till the formation of a dark blue colour. The number of c.c. used in passing from one end reaction to the other represents half of the sodium carbonate present. Other methods have been proposed by Phillips and Upward ("J.C.S.," 1886, A., pp. 920, 1074), and Isbert and Venator ("J.S.C.I.," 1888, p. 234).

Uses.—For the same purposes as potassium hydrate.

Commercial Varieties.—The chief impurity of this quality, as contrasted with the purer sorts, consists of about 1 to 2 per cent. of chloride, and generally traces of arsenic.

few drops tincture of turmeric, and evaporating to dryness on the water bath; traces of boric acid produced a cherry-red colour. The flame test was also applied. The authors came to the conclusion that the percentage of boric acid present in these samples exceeded 0·1 per cent.

Sodium Hydrate, Ordinary Commercial.—This often contains large quantities of saltpetre, purposely added during manufacture to oxidise the sodium sulphide. The metal vanadium has also been detected; and the water present often amounts to 30 per cent., although, in many cases, only a few per cent. are present. In this country the total alkalinity is expressed in degrees Na_2O, but a maximum of not more than 2 or 3 per cent. carbonate is guaranteed. In Germany only the sodium hydrate present is taken account of, but is expressed as carbonate. In France the percentage of free total alkali is recorded in degrees Descroizilles sulphuric acid, generally per 20 gms. of caustic soda. Tables for converting these degrees, and details regarding the analysis of crude caustic soda, are given in such books on the subject as Lunge's "Manufacture of Alkali and Sulphuric Acid". J. Watson ("J.S.C.I.," 1892, p. 322) has investigated the variations in the composition of caustic soda taken from the same barrel. He tested samples drawn from seven barrels, and found an average difference of 0·712 per cent. in samples drawn from the same barrel, with a maximum of 1·34 per cent. The variations, therefore, are not very great. The portions near the sides of the barrels showed the lowest, and those in the middle the highest, percentage. Caustic soda for technical purposes is sold with a guaranteed percentage.

Caustic Soda Solution.—(*a*) Liquor Natri caustic. crud. N-free (NaOH + aq.): ordinary nitrogen-free soda solution.

Clear, colourless, or slightly yellow solution. Sp. gr., 1·30, containing about 25 per cent. NaOH.

The test for nitric acid is performed as under "Potassium Hydrate, puriss."

(*b*) Liquor Natri caustic. pur. N-free: pure nitrogen-free soda solution (NaOH + aq.).

Clear, colourless liquid. Sp. gr., 1·30, containing about 27 per cent. NaOH.

It is tested as under "Sodium Hydrate, pure by Alcohol".

For table of sp. gr. of various strengths of solution, see opposite page.

Specific Gravity of Caustic Solutions at 15° (Lunge).

Sp. gr.	°B.	°Tw.	Na_2O Per Cent.	NaOH Per Cent.	1 cbm. contains kgms.	
					Na_2O.	NaOH.
1·007	1	1·4	0·47	0·61	4	6
1·014	2	2·8	0·93	1·20	9	12
1·022	3	4·4	1·55	2·00	16	21
1·029	4	5·8	2·10	2·71	22	28
1·036	5	7·2	2·60	3·35	27	35
1·045	6	9·0	3·10	4·00	32	42
1·052	7	10·4	3·60	4·64	38	49
1·060	8	12·0	4·10	5·29	43	56
1·067	9	13·4	4·55	5·87	49	63
1·075	10	15·0	5·08	6·55	55	70
1·083	11	16·6	5·67	7·31	61	79
1·091	12	18·2	6·20	8·00	68	87
1·100	13	20·0	6·73	8·68	74	95
1·108	14	21·6	7·30	9·42	81	104
1·116	15	23·2	7·80	10·06	87	112
1·125	16	25·0	8·50	10·97	96	123
1·134	17	26·8	9·18	11·84	104	134
1·142	18	28·4	9·80	12·64	112	144
1·152	19	30·4	10·50	13·55	121	156
1·162	20	32·4	11·14	14·37	129	167
1·171	21	34·2	11·73	15·13	137	177
1·180	22	36·0	12·33	15·91	146	188
1·190	23	38·0	13·00	16·77	155	200
1·200	24	40·0	13·70	17·67	164	212
1·210	25	42·0	14·40	18·58	174	225
1·220	26	44·0	15·18	19·58	185	239
1·231	27	46·2	15·96	20·59	196	253
1·241	28	48·2	16·76	21·42	208	266
1·252	29	50·4	17·55	22·64	220	283
1·263	30	52·6	18·35	23·67	232	299
1·274	31	54·8	19·23	24·81	245	316
1·285	32	57·0	20·00	25·80	257	332
1·297	33	59·4	20·80	26·83	270	348
1·308	34	61·6	21·55	27·80	282	364
1·320	35	64·0	22·35	28·83	295	381
1·332	36	66·4	23·20	29·93	309	399
1·345	37	69·0	24·20	31·22	326	420
1·357	38	71·4	25·17	32·47	342	441
1·370	39	74·0	26·12	33·69	359	462
1·383	40	76·6	27·10	34·96	375	483
1·397	41	79·4	28·10	36·25	392	506
1·410	42	82·0	29·05	37·47	410	528
1·424	43	84·8	30·08	38·80	428	553
1·438	44	87·6	31·00	39·99	446	575
1·453	45	90·6	32·10	41·41	466	602
1·468	46	93·6	33·20	42·83	487	629
1·483	47	96·6	34·40	44·38	510	658
1·498	48	99·6	35·70	46·15	535	691
1·514	49	102·8	36·90	47·60	559	721
1·530	50	106·0	38·00	49·02	581	750

SODIUM NITRATE.—Natrium nitric. puriss. ($NaNO_3$). Mol. wt., 85·01. Colourless rhombohedral crystals, giving a clear solution with water (soluble 1 : 1·2). The salt absorbs moisture from the atmosphere.

Tests for Impurities.—The tests for solubility, sulphuric acid, etc., are the same as under the potassium salt, p. 265.

Potash.—By the flame test.

Note.—A good reagent for the detection of potassium in both the nitrate and nitrite may be prepared as follows:[1] A solution of 20 gms. pure nitrite of soda in 40 to 50 c.c. of water, previously acidified with a little acetic acid, is added to a solution of 10 gms. crystallised acetate of cobalt in 25 c.c. of water. If the mixture becomes turbid owing to the presence of potash or ammonia salt (as sometimes happens even with sodium nitrite, puriss.) the solution is heated gently and filtered; after standing for a few hours, the reagent is ready for use. In the absence of free acid, it is possible to detect 0·1 per cent. of potash with certainty. In testing sodium nitrate, 10 gms. are dissolved by heat in 10 c.c. of water, and to 1 c.c. of the filtered solution, 1 to 2 drops of the reagent are added; in the presence of potassium, the characteristic yellow crystalline precipitate of potassio-cobaltic nitrite appears. If the impurity is present in very minute quantity, the precipitate forms after standing for a time.

Quantitative Estimation.—Various methods are employed for the estimation of nitrogen in sodium nitrate (see Sutton's "Vol. Anal.," pp. 245, 259). When the sample under examination stands the foregoing tests and shows freedom from potash salt, a quantitative estimation is generally superfluous; an estimation of the moisture present might be necessary, however, and this may be done by carefully heating 5 gms. in a roomy platinum capsule, and noting the loss in weight. For the valuation of commercial nitrate of soda (also the determination of the perchlorate present), see Pauli, "J.S.C.I.," 1897, p. 494; see also under "Potassium Nitrate".

Uses and Storage.—See p. 266. Owing to its hygroscopic nature, bottles containing the salt must have well-fitting stoppers.

Commercial Varieties.—The crude salt is also sold, in the form of blocks (caliche); this contains from 36 to 60 per cent. pure salt. The quality obtained from manure works contains about 95 per cent., and the purified nitre up to 99 per cent.

[1] Gilbert, "Zeit. f. angew. Chem.," 1894, p. 122.

Indirect Methods.			Direct Methods.		
A. By Difference.		B. Quartz Method (Maercker-Absser).	C. Lunge's Nitrometer.	D. Schloesing-Grandeau (Wagner's Modification).	E. Ulsch's Method.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
(1) 15·83 per cent. N = 96·10 per cent. $NaNO_3$	Water . 2·33 Insoluble 0·06 NaCl . 1·26 Na_2SO_4 . 0·25 3·90	15·59N = 94·65 $NaNO_3$	15·57N = 94·53 $NaNO_3$	15·54N = 94·35 $NaNO_3$	15·55N = 94·41 $NaNO_3$
(2) 15·84 per cent. N = 96·17 per cent. $NaNO_3$	Water . 2·15 Insoluble 0·11 NaCl . 1·18 Na_2SO_4 . 0·39 3·83	15·64N = 94·96 $NaNO_3$	15·61N = 94·77 $NaNO_3$	15·63N = 94·90 $NaNO_3$	15·62N = 94·84 $NaNO_3$
(3) 15·84 per cent. N = 96·14 per cent. $NaNO_3$	Water . 2·23 Insoluble 0·12 NaCl . 1·17 Na_2SO_4 . 0·34 3·86	15·62N = 94·84 $NaNO_3$	15·62N = 94·84 $NaNO_3$	15·63N = 94·90 $NaNO_3$	15·61N = 94·77 $NaNO_3$
(4) 15·80 per cent. N = 95·95 per cent. $NaNO_3$	Water . 2·35 Insoluble 0·09 NaCl . 1·29 Na_2SO_4 . 0·32 4·05	15·65N = 95·02 $NaNO_3$	15·63N = 94·90 $NaNO_3$	15·56N = 94·47 $NaNO_3$	15·61N = 94·75 $NaNO_3$
(5) 15·84 per cent. N = 96·14 per cent. $NaNO_3$	Water . 2·40 Insoluble 0·10 NaCl . 1·02 Na_2SO_4 . 0·34 3·86	15·56N = 94·47 $NaNO_3$	15·59N = 94·65 $NaNO_3$	15·64N = 94·96 $NaNO_3$	15·64N = 94·96 $NaNO_3$
(6) 15·65 per cent. N = 95·01 per cent. $NaNO_3$	Water . 3·18 Insoluble 0·13 NaCl . 1·32 Na_2SO_4 . 0·36 4·99	15·47N = 93·93 $NaNO_3$	15·47N = 93·93 $NaNO_3$	15·44N = 93·74 $NaNO_3$	15·43N = 93·68 $NaNO_3$

Potassium nitrate, calculated from direct estimation of the potash, was found in the following percentages in the samples: (1) 7·21, (2) 4·66, (3) 5·02, (4) 5·47, (5) 5·11, (6) 5·18.

Numerous articles have appeared of recent years regarding the presence of potash. In many instances this reaches several per cent., and in a few cases the amount found has been abnormally high. For investigations on this point, see Jones, "Zeit. f. angew. Chem.," 1893, p. 696. Alberti and Hempel ("Zeit. f. angew. Chem.," 1892, No. 4) give the results (see p. 311) obtained on analysis of six samples by several direct and indirect methods.

SODIUM NITRITE.—Natrium nitrosum, puriss. ($NaNO_2$). Mol. wt., 68·93. Colourless crystals, or thin white sticks, giving a clear solution with water (1 : 2) and containing about 99 per cent. $NaNO_2$.

Tests for Impurities and Quantitative Estimation.—See "Potassium Nitrite," p. 266. Potash may be detected by the method given under "Sodium Nitrate".

Uses.—The salt is used chiefly in organic synthesis, and also for the identification of antipyrine. Thiele describes an easy method for preparing nitric oxide from sodium nitrite ("J.S.C.I.," 1889, p. 1010).

Commercial Varieties.—The commercial preparation can now be obtained in a very pure condition, and is used for the manufacture of azo dyes, etc., the percentage guaranteed being often as high as 97 or 98 per cent. Landolt gives the following analysis as representing the average composition of commercial samples:—

	Per Cent.
Sodium nitrite	94·14
„ nitrate	2·38
„ sulphate	1·20
„ chlorate	0·06
Insoluble	traces
Water	2·08
	99·86

Note.—The water was estimated by heating at 130°, the chlorine and sulphuric acid in the usual way, the total nitrogen by Lunge's nitrometer, and after deducting the nitrogen equivalent to 94·14 of nitrite from this, that which remained was calculated to sodium nitrate (Lunge, "Zeit. f. angew. Chem.," 1891, p. 633).

SODIUM NITROPRUSSIDE.—Natrium nitro-prussic. cryst. ($Na_4Fe_2(CN)_{10}(NO)_2$, $4H_2O$). Mol. wt., 595·91. Large, ruby-red rhombic crystals, giving a clear solution with water (soluble 1 : 2·5).

Tests for Impurities.—*Sulphuric Acid.*—An aqueous solution (1 : 50) should show only a slight turbidity on adding a little hydrochloric acid and barium chloride.

Quantitative Estimation.—The general appearance of the salt presents a good guide as to its quality; the crystals ought to have the appearance quoted, and be tested for solubility in water, and for sulphuric acid. The reaction towards alkaline sulphides must also be observed. On adding a few drops of hydrogen sulphide water to a few drops of the dilute solution, with a little caustic soda, the well-known red colour must appear. Crystals of saltpetre present may be detected by the eye, thus rendering a special quantitative examination unnecessary.

Uses.—The compound is used as a delicate test for hydrogen sulphide and alkaline sulphides. Kral ("Pharm. Centralhalle," 1896, p. 69; Geissler, *ibid.*, p. 90) recommends a paper saturated with an ammoniacal solution of the salt instead of the ordinary lead paper as a test for hydrogen sulphide. Brunner ("J.S.C.I.," 1889, p. 920) uses it as a test for caustic alkali and alkaline earths; see also Béla von Bittó ("J.S.C.I.," 1892, p. 846) regarding its use as a test for aldehydes, ketones, and other organic compounds. See also V. Arnold on the reaction of proteins with nitroprusside, "Z. Physiol. Chem.," 1911, 70, pp. 300-309; "J.S.C.I.," 1911, p. 242.

Commercial Varieties.—The crystals are sometimes badly formed, and show a large percentage of sulphate.

SODIUM PEROXIDE (Na_2O_2).—Mol. wt., 78. Its properties and uses for analytical purposes are described under "Hydrogen Peroxide," p. 139.

SODIUM PHOSPHATE.—Natrium phosphoricum, puriss. (Na_2HPO_4, $12H_2O$). Mol. wt., 358·24. Colourless, transparent (monoclinic) crystals, giving a clear solution with water (soluble Na_2HPO_4 1 : 16) and showing a slight alkaline reaction.

Tests for Impurities.—*Appearance.*—The crystals must be transparent and show no sign of efflorescence.

Arsenic.—2 gms. are submitted to Marsh's test, as described under "Sodium Carbonate, chemically pure cryst.," p. 297. The test for heavy metals, etc., is also made with 2 gms., as under "Sodium Carbonate".

Sulphate and Carbonate.—The aqueous solution (1 : 20) must show no effervescence on acidifying with hydrochloric acid, and must give no reaction, even after long standing with barium chloride.

Note.—Geissler ("Pharm. Centralhalle," 1893, No. 51), on testing with phenolphthalein, found traces of carbonate in all the commercial samples. The salt, when free from this impurity, has no effect on that indicator, but if as little as 0·1 per cent. carbonate is present a red colour appears.

Chloride.—The aqueous solution, after acidifying with nitric acid, ought only to show a slight opalescence with silver nitrate.

Nitrate.—2 gms. are dissolved in 10 c.c. of water, acidified with dilute sulphuric acid, and 1 drop of indigo solution, diluted with twice its volume of water, and 10 c.c. concentrated sulphuric acid are added; the solution must retain its blue colour, even after long standing.

Potash.—By the flame test (see note, "Sodium Bicarbonate, puriss.").

Quantitative Estimation.—A solution of 20 gms. of the salt in a litre of water is prepared and 10 c.c. to 20 c.c. drawn off, and the phosphoric acid estimated in ammoniacal solution with magnesia mixture (see p. 182). After standing 12 hours the precipitate is filtered off, washed with dilute ammonia, dried, ignited, and weighed as magnesium pyrophosphate. The phosphoric acid may also be estimated by standard uranium solution. Both methods are described in books on technical analysis.

Uses.—The salt is used for the detection and estimation of magnesia, and in the testing of alkaline earths in general; also for the recovery of molybdic acid from its solution, and, when free from efflorescence, as a standard for uranium solutions Mohr prefers to use microcosmic salt for the last-mentioned

purpose (p. 285), as it does not absorb carbonic acid, and does not effloresce. According to Mohr, sodium phosphate shows this tendency, even when carefully protected from the atmosphere. Meineke ("Chem.-Ztg.," 1896, p. 109) found Merck's preparation to be very pure and to show no evidence of having lost water of crystallisation; this reputed disadvantage has therefore been rather exaggerated.

Commercial Varieties. — These consist of a variety of qualities, the cheaper samples often containing considerable quantities of sodium sulphate and arsenic.

SODIUM PYROPHOSPHATE.—Natrium pyrophosphoric. puriss. ($Na_4P_2O_7$, $10H_2O$). Mol. wt., 446·24. Colourless, monoclinic transparent crystals, giving a clear solution with water (soluble, $Na_4P_2O_7$ 1 : 11) and an alkaline reaction (the normal salt is always strongly alkaline towards litmus).

Tests for Impurities.—*Sodium Phosphate.*—Addition of silver nitrate to the solution must produce a pure white precipitate, and the filtrate ought to be neutral if all the pyrophosphate has been precipitated.

Note.—Sodium phosphate gives a yellow precipitate.

Other Salts.—See "Sodium Phosphate," p. 314.

Quantitative Estimation.—A solution of the salt is boiled with nitric acid to convert the pyrophosphoric into phosphoric acid, and after rendering alkaline with excess of ammonia, the estimation is proceeded with as under "Sodium Phosphate".

Uses.—The salt is used for the electrolytic estimation and separation of the metals ("Zeit. f. anal. Chem.," 1889, p. 581 *et seq.*; and also "J.S.C.I.," 1888, p. 401).

Commercial Varieties. — These consist of the ordinary crystal, the pure crystal, and the fused preparations; as they are prepared from sodium phosphate the impurities present are naturally the same as in the latter.

SODIUM SUCCINATE.—Natrium succinum.

$$Na_2C_4H_4O_4 + 6H_2O.$$

Mol. wt., 270·15. White crystals, slightly soluble in water.

Uses.—Employed in the separation of iron and alumina

from manganese, zinc, nickel, and cobalt (Fresenius, "Chemical Analysis, Quantitative," 7th ed., vol. i., p. 440).

SODIUM SULPHATE.—Natrium sulphuric. puriss. (Na_2SO_4, $10H_2O$). Mol. wt., 322·22. Colourless, monoclinic crystals, liable to effloresce, and soluble in 3 parts cold water (Na_2SO_4 1 : 7).

Tests for Impurities.—*Solubility, Chlorides, Metals, etc.*—The solution of 5 gms. in 50 c.c. of water must be clear and neutral, and not affected by the following reagents: Silver nitrate, hydrogen sulphide, ammonia, sodium phosphate.

Arsenic.—2 gms. by Marsh's test, as under "Sodium Carbonate," p. 297.

Quantitative Estimation.—See "Sodium Bisulphate," p. 293.

Commercial Varieties.—Ordinary commercial samples may contain the following impurities: Arsenic, zinc sulphate, magnesium sulphate, and sodium chloride.

SODIUM HYDROSULPHIDE SOLUTION.—Natrium hydrosulphurat. puriss. solut. (NaHS + aq.). A clear, colourless solution, tested and stored like the corresponding potassium salt. If the preparation is colourless, it is sufficiently free from polysulphides. Admixture with acid must produce a copious evolution of hydrogen sulphide, but no precipitate must form.

Quantitative Estimation.—See "Sodium Sulphide," below.

Uses.—See "Sodium Sulphide," below.

SODIUM SULPHIDE.—Natrium sulphurat. puriss. cryst. (Na_2S, $9H_2O$). Mol. wt., 240·20. Yellowish, or slightly brownish-yellow crystals. Very deliquescent and easily soluble in water.

Tests for Impurities.—The solution must be clear and colourless, and on addition of acid no sulphur must be precipitated, only a slight opalescence being permitted.

Quantitative Estimation.—The same method as that given under "Ammonium Sulphide" may be used. Another method, applicable to all sulphur compounds where the sulphur is capable of being converted into hydrogen sulphide, consists in

adding excess of standard potassium arsenite to the sodium sulphide solution, and then hydrochloric acid, drop by drop, till slightly acid. The sulphur is precipitated as arsenic sulphide, and on titrating a measured quantity of the clear liquid with standard iodine solution, the quantity of arsenite required for combination may be found, from which the percentage of sulphur present can be calculated (see Sutton's "Vol. Anal.," p. 329).

Uses and Storage.—In qualitative or quantitative analysis either sodium hydrosulphide or sodium sulphide solution may be used for the separation of copper sulphide from that of arsenic, antimony, or tin. A standard solution of sodium sulphide is used volumetrically for the estimation of copper, zinc, and some other metals; the preparation of this solution, which is used particularly for zinc estimations, is as follows: 600 c.c. of pure caustic soda solution (sp. gr., 1·15) are completely saturated with hydrogen sulphide, and more soda solution added until the smell of the gas can no longer be detected. The solution is finally diluted and tested on a zinc solution of known strength, and is generally so standardised that 1 c.c. equals 0·005 or 0·01 gm. zinc (Schaffner, "Zeit. f. angew. Chem.," 1892, p. 166). Sodium sulphide, like the ammonium or potassium compound, decomposes in contact with the atmosphere, and must therefore be well protected.

Commercial Varieties.—Crude sodium sulphide is used in the tanning and bleaching industries. The commercial preparation is, as a general rule, very pure.

SODIUM SULPHITE, $Na_2SO_3 7H_2O$. — See "Bisulphite," p. 293.

SODIUM THIOANTIMONIATE.—Sodium Sulphantimoniate. Schlippe's Salt. $Na_3SbS_4 + 9H_2O$. Mol. wt., 433·58. Large colourless or yellow tetrahedrons.

Uses.—Is employed in the detection of alkaloids with which it gives coloured precipitates.

SODIUM THIOSULPHATE. — Natrium hyposulphuros. puriss.: hyposulphite of sodium ($Na_2S_2O_3$, $5H_2O$). Mol. wt.,

248·2. Colourless, transparent monoclinic crystals. (Soluble in water 1 : 1·4.)

Tests for Impurities.—*Sodium Sulphate and Sulphite.*—3 gms. dissolved in about 50 c.c. of water, and oxidised with iodine, must not show a turbidity with barium chloride.

Note.—In making a qualitative test even a large quantity of the salt must fail to give this reaction. Testing directly with barium chloride is inaccurate, as Fresenius and Salzer have shown that both carbonate and sulphate of barium are very soluble in the thiosulphate solution (Meineke, "Chem.-Ztg.," 1894, p. 33).

Free Alkali.—The solution (1 : 10) must be clear and show no red colour, or only a faint tinge, with phenolphthalein.

Lime.—No turbidity should appear on addition of ammonia and ammonium oxalate to the solution (1 : 20).

Quantitative Estimation.—A solution of 25 gms. in a litre of water is made, of which 25 c.c. are drawn off and titrated with $\frac{n}{10}$ iodine solution, with starch as indicator. 1 c.c. equals 0·02482 gm. $Na_2S_2O_3, 5H_2O$.

Uses and Storage.—The salt is used for the preparation of a decinormal solution employed in chlorine and iodine estimations. G. Topf ("J.C.S.," 1887, A., pp. 688, 997) has analysed various commercial samples, and in nearly every case reports favourably as to their purity. In consequence of the moisture adhering to the crystals only about 98 per cent. is found on titration with iodine, a fact which must be taken into account when preparing the decinormal solution. About 1 gm. in excess of the quantity required should always be weighed out, and a litre must contain 24·82 gms. of the pure salt. Its preparation is described in Sutton's "Vol. Anal.," p. 130. The solution alters in strength through time, especially in presence of light. Regarding the stability of thiosulphate solutions, Salzer has published the following ("J.S.C.I.," 1893, p. 182):—

(1) A $\frac{n}{10}$ thiosulphate solution, when properly prepared from a chemically pure salt and carefully preserved, may be used as a standard, so long as no reaction is obtained with barium nitrate after addition of iodine solution in slight excess.

(2) The solution may be kept in an almost perfect state of preservation for a long time (five years) by the addition of 0·2 per cent. of ammonium carbonate, but will be reliable only

when different methods giving concordant results have been used to find its strength, and so long as no reaction with barium nitrate can be detected.

SODIUM THIOSULPHATE, 100 per cent.—According to Meineke, loc. cit., a salt, the solution of which will show a correct and constant titre, may be prepared by triturating the almost pure crystals with 96 per cent. alcohol, removing the alcohol by washing with absolute alcohol and ether, and drying between filter paper; a preparation freed from water in this way showed, during a period of five years, a percentage of from 99·90 to 99·94 of $Na_2S_2O_3, 5H_2O$.

Commercial Varieties.—See under "Uses".

SODIUM TUNGSTATE.—Natrium wolframic. puriss. ($Na_2WO_4, 2H_2O$). Mol. wt., 330·03. Colourless rhombic crystals, giving a clear solution with water. (Soluble 1 : 4.)

Tests for Impurities.—*Chloride and Sulphate.*—The solution (1 : 20) is boiled with nitric acid, filtered, and to a portion of the filtrate a few drops of silver nitrate solution are added; only a slight turbidity should appear. Another portion should behave likewise towards barium chloride.

Note.—On the detection of molybdic acid, see "Commercial Varieties".

Quantitative Estimation.—The salt is first of all decomposed with hydrochloric acid and the acid completely driven off at from 120° to 125°; the chloride thus formed is dissolved in water and filtered; the tungstic acid is then washed with dilute potassium nitrate solution, and after removing the latter by washing with water containing nitric acid, the tungstic acid may be estimated gravimetrically.

Uses.—The salt is used for the preparation of sodium phosphotungstate and cadmium boro-tungstate (see latter, p 63).

Commercial Varieties, Tungstic Acid, etc.—Sodium tungstate is sold in various forms; the cheap commercial qualities of low percentage contain generally large quantities of the chloride, sulphate, and carbonate, the author having found a sample to contain 30 per cent. of crystallised carbonate. The better quality used for analytical purposes should show only a

slight alkaline reaction. Friedheim, Traube, and others ("Zeit. f. anorg. Chem.," vol. i., No. 1, p. 76) found molybdic acid present in the commercial varieties, and particularly in tungstic acid, puriss., which contained it in every instance. Traube found 10 per cent. of this impurity in the commercial tungstic acid. On the detection of the foregoing impurities, and the preparation of the acid absolutely free from molybdic acid, see "Zeit. f. anorg. Chem.," loc. cit.

STARCH (AMYLUM), $C_6H_{10}O_5$ + Aq.—This is a white powder, used for the preparation of the ordinary starch solution, for which purpose it is mixed with a little cold water to form a paste, and then, while stirring, 100 parts of boiling water are added. This solution gives a blue colour with iodine; it decomposes on keeping. For zinc iodide solution, see later.

STARCH, SOLUBLE (AMYLUM SOLUBLE).—This is a white powder, completely soluble in water, prepared by treatment of starch with acids, etc. It is used for determining the diastatic power of malt and diastase, and is employed for this purpose in the form of a 2 per cent. solution in water (see C. J. Lintner, "The Brewing Trade Review," April, 1887, p. 204). Soluble starch must be free from acid, and must not reduce Fehling's solution, or but slightly, as only traces of sugar are permitted. For the preparation of soluble starch, see Wroblewski, "J.S.C.I.," 1897, p. 1028.

SUGAR.—Glucose, grape sugar ($C_6H_{12}O_6$), and saccharose, or cane sugar ($C_{12}H_{22}O_{11}$), are those chiefly used for analytical purposes.

1. Grape Sugar, Anhydrous.—Pure white powder, or fine white crystalline crusts (Soxhlet's grape sugar).

Tests for Impurities.—*Solubility, etc.*—The solution (1 : 10) must be clear and colourless, or only show a slight yellow-wine colour, and have no action on litmus paper.

Sulphates, Chlorides.—The solution (1 : 20) must show no turbidity with either barium or silver nitrate.

Residue.—On igniting 1 gm. in a platinum capsule no residue must remain behind.

Melting Point.—146° C.

Note.—When water is present, the sugar melts below 100°.

Quantitative Estimation.—The sugar may be determined quantitatively by Fehling's solution (see Sutton's "Vol. Anal.," p. 305 *et seq.*).

2. Saccharose.—Colourless monoclinic crystals, or pure white powder. Soluble in water (1 : 0·5), only very sparingly in alcohol. Its preparation is given under "Fehling's Solution," p. 109.

Tests for Impurities.—As under "Grape Sugar".

Quantitative Estimation.—As under "Fehling's Solution," or by the polariscope. On uses of saccharose, see "Fehling's Solution".

Commercial Varieties.—The above refers to chemically pure sugar. The commercial varieties are exhaustively treated of in Allen's "Comm. Organ. Anal.," vol. i., p. 300 *et seq.*

SULPHANILIC ACID.—Acid. sulphanilicum cryst.

$$(NH_2C_6H_4SO_3H, 2H_2O).$$

Mol. wt., 209·19. White, needle-like crystals, difficultly soluble in water and quickly efflorescing. One part of the acid is soluble in 166 parts of water at 10°. The crystals are carbonised on heating to a temperature of 280° to 300°.

Tests for Impurities and Quantitative Estimation.—The purity may be gauged from general appearance, solubility in water, and behaviour on volatilisation.

The preparation must be free from sulphuric acid. On the quantitative estimation, see, *inter alia*, Böckmann, "Chem.-techn. Untersuch.," 3rd ed., vol. ii., p. 57.

Uses.—It is used in conjunction with naphthylamine sulphate as a test for nitrous acid and nitrites (Peter Griess, "J.C.S.," 1881, p. 231; Sutton's "Vol. Anal.," p. 436).

Commercial Varieties.—The acid, when purchased, shows more or less evidence of efflorescence, but is generally pure.

6-SULPHO-β-NAPHTHOLAZO-m-OXYBENZOIC ACID.—This compound is very similar to litmus in its behaviour to acids and alkalies, but according to R. Mellet ("Chem. Zeit.," 1910, p. 1073; Merck's "Annual," 1910, p. 357) it is 30 times more intense in colour, and is sufficiently sensitive to be used for 1/100

normal solutions. With alkalies it yields a deep violet colour which changes to an orange red on addition of acids.

SULPHURIC ACID.—Acid. sulphuric. puriss. (H_2SO_4). Mol. wt., 98·08. A clear, colourless liquid. Sp. gr., 1·84.

Note.—A commercial acid which shows any turbidity should be rejected at once.

Tests for Impurities.—*Residue.*—10 gms. must not leave any weighable residue on evaporation and ignition in a platinum capsule.

General Appearance.—The acid must be clear and colourless and must not give a blue colour with diphenylamine (see "Diphenylamine").

Note.—The diphenylamine reaction is not confined to nitric acid, but may also be obtained in presence of such compounds as potassium chlorate, potassium permanganate, molybdic acid, and ferric sulphate in acid solution, etc. ("Rep. d. Chem.-Ztg.," 1887, p. 256; and "J.S.C.I.," 1885, p. 613).

According to Lunge ("Chem. Industrie," 1888, p. 209; and "J.S.C.I.," 1887, p. 679) sulphuric acid containing selenium will also show the colour. On the application of the diphenylamine test, see Egger, "Chem.-Ztg.," 1887, p. 1500, and on the sensitiveness of nitric acid reactions, see "Chem. Industrie," 1888, pp. 140, 141. The absence of nitro-compounds from sulphuric acid is not only of importance as regards the brucine and diphenylamine reactions, but also in testing for furfurol with naphthol-sulphuric acid. (Furfurol may be detected in glycerine, for example, as follows: 1 c.c. of glycerine is mixed with 1 c.c. of water, and 2 drops of a 2 per cent. α-naphthol solution in alcohol added, then 15 drops of the pure sulphuric acid are allowed to run slowly down the sides of the test tube, in order to form a layer below the mixture.) If the acid is not perfectly free from nitro-compounds, a green colour appears.

Selenium.—To 2 c.c. of the sample 2 c.c. of hydrochloric acid, containing a little sodium sulphite, are carefully added so as to form a layer; neither a red zone nor a reddish precipitate on heating must appear.

Reducing Substances.—60 c.c. of water are added to 15 c.c. of the acid, the solution is cooled, and 1 drop of $\frac{n}{10}$ permanganate is added; the solution must remain distinctly red for a few minutes.

Lead.—On mixing the acid with 5 times its volume of strong alcohol no turbidity must appear, even after long standing.

Other Metals.—10 c.c. of the acid are diluted with water, ammonia added in excess, and a few drops of ammonium sulphide and ammonium oxalate; no greenish colour or turbidity must appear. 20 c.c. are diluted with 100 c.c. of water; this solution must neither turn brown nor deposit brown flakes on standing after passing hydrogen sulphide.

Note.—Acid containing tin is sometimes found, showing a heavy brownish precipitate with hydrogen sulphide; the latter, however, will not detect traces of lead. These can be found on testing with alcohol.

Arsenic.—20 gms. of arsenic-free zinc are placed in a Marsh apparatus of 200 c.c. capacity, and the sulphuric acid, diluted with 3 times its volume of water, added; no arsenical mirror must have appeared after the apparatus has been working for half an hour.

Note.—A chemically pure acid, standing the above test, can easily be obtained, but the author has found several samples of this description to contain lead and to reduce permanganate. It must be observed that Marsh's test is not reliable in presence of sulphurous, nitrous, and nitric acids, and in such cases either the tin method, or Hager's "Kramato" method are preferable (Böckmann, "Chem.-techn. Untersuch.").

The estimation may also be carried out by the process adopted in the "British Pharmacopœia," 1914, p. 501, the solution being treated with arsenic free zinc, and the hydrogen, first passed over lead acetate paper, being allowed to act on mercuric chloride paper, which is coloured more or less if arsenic is present, the colours being matched against known quantities of arsenic. This is an extremely sensitive test.

Ammonia.—2 gms. are diluted with about 30 c.c. of water, an excess of a solution containing from 3 to 4 gms. pure caustic potash added; after cooling, 10 or 15 drops of Nessler's reagent are added; no yellow or brownish-red colour must appear.

Note.—W. Gintl found 5 per cent. of ammonia in a commercial acid. sulphuric. puriss. Nessler's test is very reliable, as the author obtained a distinct yellow colour and turbidity on adding 1 mgm. of ammonia to 100 c.c. of acid, and testing as above.

Halogens.—On diluting 2 gms. to 30 c.c. and adding a few drops of silver nitrate solution, no precipitate must appear.

Quantitative Estimation.—The specific gravity is estimated

by Mohr's balance; the percentage may then be found by means of the following table :—

TABLE SHOWING THE SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° (KOLB).

°B.	Sp. gr.	100 Parts by Weight Contain				A Litre Contains Kgms.			
		SO_3 Per Cent.	H_2SO_4 Per Cent.	Acid of 60° B.	Acid of 53° B.	SO_3.	H_2SO_4.	Acid of 60° B.	Acid of 53° B.
0	1·000	0·7	0·9	1·2	1·3	0·007	0·009	0·012	0·013
1	1·007	1·5	1·9	2·4	2·8	0·015	0·019	0·024	0·028
2	1·014	2·3	2·8	3·6	4·2	0·023	0·028	0·036	0·042
3	1·022	3·1	3·8	4·9	5·7	0·032	0·039	0·050	0·058
4	1·029	3·9	4·8	6·1	7·2	0·040	0·049	0·063	0·074
5	1·037	4·7	5·8	7·4	8·7	0·049	0·060	0·077	0·090
6	1·045	5·6	6·8	8·7	10·2	0·059	0·071	0·091	0·107
7	1·052	6·4	7·8	10·0	11·7	0·067	0·082	0·105	0·123
8	1·060	7·2	8·8	11·3	13·1	0·076	0·093	0·120	0·139
9	1·067	8·0	9·8	12·6	14·6	0·085	0·105	0·134	0·156
10	1·075	8·8	10·8	13·8	16·1	0·095	0·116	0·148	0·173
11	1·083	9·7	11·9	15·2	17·8	0·105	0·129	0·165	0·193
12	1·091	10·6	13·0	16·7	19·4	0·116	0·142	0·182	0·211
13	1·100	11·5	14·1	18·1	21·0	0·126	0·155	0·199	0·231
14	1·108	12·4	15·2	19·5	22·7	0·137	0·168	0·216	0·251
15	1·116	13·2	16·2	20·7	24·2	0·147	0·181	0·231	0·270
16	1·125	14·1	17·3	22·2	25·8	0·159	0·195	0·250	0·290
17	1·134	15·1	18·5	23·7	27·6	0·172	0·210	0·269	0·313
18	1·142	16·0	19·6	25·1	29·2	0·183	0·224	0·287	0·333
19	1·152	17·0	20·8	26·6	31·0	0·196	0·233	0·306	0·357
20	1·162	18·0	22·2	28·4	33·1	0·209	0·258	0·330	0·385
21	1·171	19·0	23·3	29·4	34·8	0·222	0·273	0·349	0·407
22	1·180	20·0	24·5	31·8	36·6	0·236	0·289	0·370	0·432
23	1·190	21·1	25·8	33·0	38·5	0·251	0·307	0·393	0·458
24	1·200	22·1	27·1	34·7	40·5	0·265	0·325	0·416	0·446
25	1·210	23·2	28·4	36·4	42·4	0·281	0·344	0·440	0·513
26	1·220	24·2	29·6	37·9	44·2	0·295	0·361	0·463	0·539
27	1·231	25·3	31·0	39·7	46·3	0·311	0·382	0·489	0·570
28	1·241	26·3	32·2	41·2	48·1	0·326	0·400	0·511	0·597
29	1·252	27·3	33·4	42·8	49·9	0·342	0·418	0·536	0·625
30	1·263	28·3	34·7	44·4	51·8	0·357	0·438	0·561	0·654
31	1·274	29·4	36·0	46·1	53·7	0·374	0·459	0·587	0·684
32	1·285	30·5	37·4	47·9	55·8	0·392	0·481	0·616	0·717
33	1·297	31·7	38·8	49·7	57·9	0·411	0·503	0·645	0·751
34	1·308	32·8	40·2	51·1	60·0	0·429	0·526	0·674	0·850
35	1·320	33·8	41·6	53·3	62·1	0·447	0·549	0·704	0·820
36	1·332	35·1	43·0	55·1	64·2	0·468	0·573	0·734	0·856
37	1·345	36·2	44·4	56·9	66·3	0·487	0·597	0·765	0·892
38	1·357	37·2	45·5	58·3	67·9	0·505	0·617	0·791	0·921
39	1·370	38·3	46·9	60·0	70·0	0·525	0·642	0·822	0·959

°B.	Sp. gr.	100 Parts by Weight Contain.				A Litre Contains Kgms.			
		SO_3 Per Cent.	H_2SO_4 Per Cent.	Acid of 60° B.	Acid of 53° B.	SO_3.	H_2SO_4.	Acid of 60° B.	Acid of 53° B.
40	1·383	39·5	48·3	61·9	72·1	0·546	0·668	0·856	0·997
41	1·397	40·7	49·8	63·8	74·3	0·569	0·696	0·891	1·038
42	1·410	41·8	51·2	65·6	76·4	0·589	0·722	0·925	1·077
43	1·424	42·9	52·8	67·4	78·5	0·611	0·749	0·960	1·108
44	1·438	44·1	54·0	69·1	80·6	0·634	0·777	0·994	1·159
45	1·453	45·2	55·4	70·9	82·7	0·657	0·805	1·030	1·202
46	1·468	46·4	56·9	72·9	84·9	0·681	0·835	1·070	1·246
47	1·483	47·6	58·3	74·7	87·0	0·706	0·864	1·108	1·290
48	1·498	48·7	59·6	76·3	89·0	0·730	0·893	1·143	1·330
49	1·514	49·8	61·0	78·1	91·0	0·754	0·923	1·182	1·378
50	1·530	51·0	62·5	80·0	93·3	0·780	0·956	1·224	1·427
51	1·540	52·2	64·0	82·0	95·5	0·807	0·990	1·268	1·477
52	1·563	53·5	65·5	83·9	97·8	0·836	1·024	1·311	1·529
53	1·580	54·9	67·0	85·8	100·0	0·867	1·059	1·355	1·580
54	1·597	56·0	68·6	87·8	102·4	0·894	1·095	1·402	1·636
55	1·615	57·1	70·0	89·6	104·5	0·922	1·131	1·447	1·688
56	1·634	58·4	71·6	91·7	106·9	0·954	1·170	1·499	1·747
57	1·652	59·7	73·2	93·7	109·2	0·986	1·210	1·548	1·804
58	1·672	61·0	74·7	95·7	111·5	1·019	1·248	1·599	1·863
59	1·691	62·4	76·4	97·8	114·0	1·055	1·292	1·654	1·928
60	1·711	63·8	78·1	100·0	116·6	1·092	1·336	1·711	1·995
61	1·732	65·2	79·0	102·3	119·2	1·129	1·384	1·772	2·065
62	1·753	66·7	81·7	104·6	121·9	1·169	1·432	1·838	2·137
63	1·774	68·7	84·1	107·7	125·5	1·219	1·492	1·911	2·226
64	1·796	70·6	86·5	110·8	129·1	1·268	1·554	1·990	2·319
65	1·819	73·2	89·7	114·8	138·8	1·332	1·632	2·088	2·434
66	1·842	81·6	100·0	128·0	149·3	1·503	1·842	2·358	2·750

For acids over 90 per cent., Kolb's figures are not reliable, but the table on next page by Lunge and Naef can be taken as being correct.

The figures marked with an asterisk represent actual estimations; the others are interpolated. All values given refer to chemically pure acid; with commercial qualities of highest concentration the specific gravity is greater. The more recent tables by Lunge and Isler for acids of lower concentration are also more reliable than those by Kolb, and may be found in Lunge's "Alkali-makers' Handbook," p. 100. The acid is estimated by titration with normal alkali, and the results are always given in per cent. by weight.

Table Showing the Specific Gravity of Highly Concentrated Sulphuric Acid at 15°.

H_2SO_4 Per Cent.	Sp. gr.	°B.	H_2SO_4 Per Cent.	Sp. gr.	°B.
90	1·8185	65·1	*95·97	1·8406	66·0
*90·20	1·8195		96	1·8406	
91	1·8241	65·4	97	1·8410	
*91·48	1·8271		*97·70	1·8413	
92	1·8294	65·6	98	1·8412	
*92·83	1·8334		*98·39	1·8406	
93	1·8339	65·8	*98·66	1·8409	
94	1·8372	65·9	99	1·8403	
*94·84	1·8387		*99·47	1·8395	
95	1·8390	66·0	*100·00	1·8384	

Uses, Storage and Normal Sulphuric Acid.—The pure acid is used for the detection and determination of lead and barium; also as a solvent for minerals in the analysis of soils, and for the decomposition of some organic substances. According to Plaatz ("J.S.C.I.," 1890, p. 415) an acid containing from 6 to 8 per cent. of water is said to be the most suitable for drying gases. In forensic analysis an acid free from arsenic is used in Marsh's test, and, when free from nitrogen, is used for the decomposition of the organic substance in Kjeldahl's method. For this purpose a mixture of 3 volumes concentrated and 2 volumes fuming sulphuric acid is generally taken. The concentrated acid is also used in microscopical analysis ("Zeit. f. anal. Chem.," 1886, p. 537).

The acid must be kept in glass-stoppered bottles.

Normal Sulphuric Acid.—The solution must contain 49·04 gms. H_2SO_4 per litre (see also note under "Normal Alkali," p. 257).

In order to prepare the solution, from 52 gms. to 53 gms. of the pure acid are diluted to a litre, and the strength found gravimetrically, or by titration with sodium carbonate, then water is added until the solution has attained the correct strength. König dilutes 20 c.c. of the acid with a considerable quantity of water, renders slightly alkaline with ammonia, then slightly acid with hydrochloric acid, and finally precipi-

tates with barium chloride, and calculates the strength from the weight of barium sulphate obtained.

Schaffgotsch, Eckenroth, and Weinig ("Zeit. f. anal. Chem.," 1893, p. 450) recommend evaporating down with pure ammonia and drying and weighing the residual ammonium sulphate. The author can also vouch for the simplicity and accuracy of this method. The method generally adopted in alkali works is to establish the strength on pure anhydrous sodium carbonate (see Lunge, "Alkali-maker's Handbook," p. 168); special precautions must be taken, however, when using litmus as indicator (Reinitzer, "J.C.S.," 1894, A., p. 134).

Commercial Varieties. — Regarding the impurities sometimes found in pure commercial sulphuric acid, see notes, pp. 322, 323.

SULPHURIC ACID, COMMERCIAL. — The acid may be obtained either in the concentrated form (168° Tw.), or as acid of 144° Tw. A commercial acid, free from arsenic, and also the monohydrate or 100 per cent. acid (separated out from the concentrated by freezing), may be placed under the above heading. The chief impurities of the commercial acid are: Arsenic, hydrochloric acid, lead, iron, titanium, nitric oxide, nitrous and nitric acids, selenium, and sulphurous anhydride.

Buchner ("J.S.C.I.," 1891, p. 460) found 131 gms. of arsenious acid in 100 kilos of a commercial sample, and Dott ("Pharm. Journ.," 1890, p. 475) in a similar instance detected 0·1565 gm. in 50 c.c. A good commercial acid ought not to contain more than from 0·8 to 4·4 gms. arsenic in 100 kgms. ("Chem.-Ztg.," 1891, p. 43).

The acid is often somewhat opaque. R. Norrenberg has published an article calling attention to the ruddy colour developed in crude acid containing nitrous compounds when kept in iron vessels, and has ascribed this appearance to the reducing action of gradually formed ferrous sulphate solution on the aforesaid compounds, with formation of nitric oxide. An acid free from nitrogen never turns red on keeping in iron vessels. Details regarding the quantitative estimation of the impurities in commercial acid may be found in Lunge's "Manufacture of Alkali and Sulphuric Acid," vol. i., p. 171 *et*

seq., and also the method of determining the strength by the hydrometer (*ibid.*, p. 114). According to Lunge, concentrated acids ought always to be tested volumetrically, as the impurities affect the specific gravity.

SULPHURIC ACID, FUMING.—Acid. sulphuric. fumans ($H_2SO_4 + SO_3$). Mol. wt., 178·14. Viscous liquid, fuming in contact with the atmosphere, sometimes slightly coloured and not quite transparent.

Tests for Impurities.—*Nitric Acid.*—From 3 to 4 drops of indigo solution diluted with 10 times the volume of water are added to 20 gms. of the acid, and 20 c.c. of water carefully introduced; the solution must remain blue for some time.

Note.—Fuming (Nordhausen) sulphuric acid mixed with the pure acid in the proportion of 2 to 3 is used in the Kjeldahl method, a blank test being made to prove its freedom from nitrogen. The tests for nitric acid under "Sulphuric Acid, puriss." cannot be applied in this case. The author has found a commercial sample labelled "nitrogen free," which stood the above test, but under ordinary circumstances such samples quickly decolorise from 4 to 5 drops indigo solution. In order to prove the reliability of this test, 0·0005 gm. of nitric acid was added to 20 gms. of a commercial sample, free from nitrogen; on applying the test, the indigo was at once decolorised. According to Garnier ("Rep. d. Chem.-Ztg.," 1887, p. 148) the ordinary acid often contains ammonia, to avoid which he dissolves 1 part of sulphuric anhydride in 3 parts of English sulphuric acid.

Other Impurities.—As under "Sulphuric Acid, puriss.".

Quantitative Estimation.—It is chiefly used in dye manufacture, and is generally sold according to the amount of SO_3 and H_2SO_4 present For example, an acid is called a 20 per cent. sample if it contains 20 per cent. SO_3 and 80 per cent. H_2SO_4. An accurate determination of its strength may be made by careful titration (see Lunge, "Alkali-makers' Handbook," p. 110).

Uses and Storage.—It is used in gas analysis for the absorption of the heavy hydrocarbons and for nitrogen estimations by Kjeldahl's method, as already mentioned. It is also used, as well as the pure sulphuric anhydride, in organic synthesis (see Strecker-Wislicenus, "Organic Chemistry," p. 290, trans. by Hodgkinson and Greenaway). For gas analysis the acid must be of such strength that on cooling to 0° C. crystals

of pyrosulphuric acid are deposited. It must be very carefully kept in glass-stoppered bottles.

Commercial Varieties.—Alkaline sulphates, sulphurous anhydride, nitric acid, and lead are nearly always present. The acid, also known as "Oleum," is sold according to the percentage of SO_3 present, and may easily be manufactured to contain any amount of SO_3 up to 100 per cent. A table by Winkler, giving the specific gravity and correspoding percentage of SO_3, is given in Lunge's "Manufacture of Alkali and Sulphuric Acid". The acid is simply prepared by adding SO_3 to sulphuric acid. Sulphuric anhydride is now sold in cast-iron vessels capable of acting as retorts, so that any quantity required may be distilled over into the monohydrate. It may also be obtained in small glass bottles in a fused condition ready for mixing.

SULPHUROUS ACID.—Acidum sulphurosum (SO_2 + aq.). A clear, transparent liquid, containing 6 per cent. SO_2.

The acid acts as a reducing agent, decolorising iodine solution and potassium permanganate, and converting chromic acid into chromium oxide with oxidation to sulphuric acid.

The anhydrous (100 per cent.) acid is now prepared on the large scale from kiln gases, and is used in sugar factories for the purpose of effecting an economy in animal charcoal, and also as a bleaching agent in textile industries. It can now be obtained in syphons which are very handy. The methods for its quantitative estimation are given under "Sodium Bisulphite". In solution it readily evaporates and oxidises, and ought therefore to be well stoppered and kept cool. A convenient method for the preparation of the gas for laboratory purposes is given by G. Neumann, which is as follows: Concentrated sulphuric acid is allowed to act in a Kipp's apparatus upon a mixture of 3 parts of calcium sulphite with 1 part of plaster of Paris, the latter being used merely to mould the sulphite into suitable cubes. A constant stream of gas, lasting for about 30 hours, may be obtained from 500 gms. of this mixture ("J.S.C.I.," 1887, A., p. 769).

SULPHURETTED HYDROGEN OR HYDROGEN SULPHIDE WATER.—This may be prepared by the action of

hydrochloric acid on iron sulphide in Kipp's apparatus; the gas is washed with water, and is then led into distilled water (which has been thoroughly boiled and cooled beforehand) until the latter is saturated. The solution should be kept in small, dark brown bottles in a cool place, the bottles being corked and sealed with paraffin. It should smell strongly of the gas (see also under "Iron Sulphide," p. 164). As deaths have occurred from the inhalation of H_2S it is absolutely necessary to have good ventilation in rooms where it is employed. On Jacobson and Brunn's method for the elimination of arsenic by means of iodine, see a paper by Skraup ("J.C.S.," 1897, A., ii., p. 123). On the production of pure hydrogen sulphide from calcium hydrosulphide, see Michler, "J.C.S.," A., ii., p. 290.

TANNIN.—Tannin puriss.: gall-nut tannic acid ($C_{14}H_{10}O_9$). Mol. wt., 322·15. Glistening powder, slightly buff coloured, and giving a clear solution with water (1 : 1) and with absolute alcohol.

Tests for Impurities.—*Ash.*—1 gm. must leave no weighable residue on ignition.

Solubility.—2 gms. in about 10 c.c. of alcohol must give a clear solution (absence of gum and dextrin) which must not become turbid on further addition of 10 c.c. of ether or of water (absence of rosin). The aqueous solution should be clear.

Note.—According to Vulpius ("Pharm. Centralhalle, N.F.," 1894, 15, p. 710; see also Allen's "Comm. Organ. Anal.," vol. iii., part i., p. 81) no commercial sample is absolutely free from gallic acid, and he considers the only trustworthy test for this impurity to be potassium cyanide, which gives a red colour in presence of gallic, but no reaction with tannic acid. For the estimation and separation of these two acids, see a method by Fleck and Dreaper, "Zeit. f. anal. Chem.," 1895, p. 106; see also "J.S.C.I.," 1893, p. 412. On the estimation of sugar in tanning materials, tannin extracts, etc., see an article by von Schröder, Bartel and Schmitz-Dumont ("Dingl. Polyt. Jour.," 293, pp. 229-237, 252-260). By this method the tannic acids are precipitated in the extracts with lead acetate, excess of the latter removed with sodium sulphate, and the filtrate tested with Fehling's solution. In young oak bark, these observers found an average of 2·65 per cent. of sugar, and 10·52 per cent. of tannin. In myrobalans they found 5·35 per cent. of sugar and 30 per cent. of tannin.

Quantitative Estimation.—Many methods have been proposed for the estimation of tannin, but only those based on the hide powder process have found general acceptance. The first step consists in an estimation of the tannin and extract together; the former is then precipitated with hide powder, and the extract, etc., estimated in the filtrate; the tannin is then found by difference. According to Hammer, if the specific gravity of the extract of a tanning material is taken before and after precipitation and the tannin calculated from the difference of the two gravities, the estimation is good enough for all practical purposes. Hammer has devised a table to facilitate the working of this method. Löwenthal and von Schröder titrate the extract with permanganate, using indigo as indicator, both before and after precipitation with hide powder. The gravimetric method, consisting of an estimation of the organic residue before and after treatment with hide powder, is also very satisfactory. Various processes are described in Allen's "Comm. Organ. Anal.," vol. iii., p. 107 *et seq.*

In these estimations it is a matter of great importance that only hide powder, which has been thoroughly washed free from all soluble organic substances, should be used. According to von Schröder the best hide powders, prepared from carefully washed skins, are not sufficiently pure for immediate use, but must be washed again with water. The present author's experiments have proved that a powder prepared from well-washed skin may still give from 0·04 gm. to 0·15 gm. of the above substances in 100 gms. of the filtrate, even when the skin had been carefully washed before grinding. The present author has made a number of experiments both with calf and bullock skin; these were first treated with lime, then cleaned and washed, thoroughly dried, and finally ground to a more or less fine powder. On examination the results already quoted were obtained, fully corroborating von Schröder's statement.

In the dyeing and printing industries, where tannin is chiefly used, its efficacy as a mordant constitutes the basis of valuation, instead of a direct assay. Small strips of calico of known weight are mordanted with equally strong solutions of the different tanning materials; they are then fixed with tartar emetic and dyed with fuchsine, Victoria green, or malachite

green, and the strips thus dyed are finally washed with soap. If the conditions of temperature and time employed have been identical in each case the test presents a method of comparison. The better the tannin the better the dyed calico will stand the washing, and the finer and more intense will be the colour after washing free from soap and drying. In calico printing the test is generally made with Victoria green or malachite green.

Uses.—Tannin is used as a test for iron, and forms insoluble compounds with alkaloids, albuminates, and other organic substances. It is also used as a group reagent for alkaloids. The standard solutions employed for tannin estimations are tested against the purest quality of tannin.[1]

Commercial Varieties.—Tannin of a very good quality may be obtained in the form of lumps, grain, powder, or as a loose mass. The more expensive kinds used industrially in large quantities are also of very satisfactory quality. Von Schröder found the light commercial puriss., when calculated on the dry material (at 100°), to contain from 95·20 to 100 per cent. using Hammer's hide powder method. By the same process the better class of commercial samples showed from 83·63 to 91·99 per cent., calculated on the dry substance. The percentage of water varied between 10·56 and 16·50 per cent.

TARTARIC ACID.—Acid. tartaric puriss. ($C_4H_6O_6$). Mol. wt., 150·07. Colourless and odourless monoclinic prisms, non-hygroscopic, and easily soluble in water (1 : 0·75) and alcohol (1 : 4), slightly soluble in ether. M.p., 168°.

Tests for Impurities.—*Non-Volatile Residue.*—After ignition in an open platinum dish there should be not more than a trace of ash.

Sulphuric and Oxalic Acids, Lime.—An aqueous solution (1 : 10) must give no reaction with either sulphate of lime solu-

[1] For this purpose, J. H. Vogel ("Zeit. f. angew. Chem.," 1891, p. 69) recommends purifying by repeated recrystallisations from ether, and remarks that the tannin must be perfectly free from the foreign organic matter which is present in small quantity in very many commercial samples. The author considers this recommendation useless, as tannin is, as is well known, not a crystalline, but an amorphous body.

tion, barium chloride, or, after adding excess of ammonia, ammonium oxalate.

Metals.—The aqueous solution must give no reaction with hydrogen sulphide, either before or after adding a layer of ammonia.

Note.—The various commercial varieties often contain iron, lead, lime, or sulphuric acid. Regarding the degree of delicacy of the tests given here, and which have been compiled according to the German Pharmacopœia, see "Arch. d. Pharm.," 1887, p. 653; and "Pharm. Ztg.," 1894, p. 140. Lead has often been detected in commercial samples, both combined and in the metallic state. Guillot ("J.S.C.I.," 1892, p. 838) obtained a residue consisting of pieces of wood, crystals of calcium sulphate, and metallic lead on dissolving one kilogram of a sample in boiling water. He estimated the lead and found it to amount to 0·0626 gm. This impurity originates from the lead vessels used in the manufacture. For the estimation of metallic lead in citric and tartaric acids, M. Bucket ("J.S.C.I.," 1892, p. 848) dissolves 200 gms. of the sample in 3 times this amount of water, and adds a slight excess of ammonia to make sure that any crystallised lead sulphate which may be present is dissolved. After standing for 24 hours the solution is decanted off and the residue washed and dissolved in nitric acid; the lead is then precipitated with sulphuric acid and alcohol. In the solution of ammonium citrate or tartrate the lead compounds are precipitated with hydrogen sulphide, after acidifying with hydrochloric acid. The lead may also be estimated by the limit test of the "British Pharmacopœia," 1914, p. 497, in which it is determined colorimetrically by means of Na_2S in presence of KCN and comparison with a standard solution of lead nitrate. Limits are given for various chemicals, that for tartaric acid, being 20 pts. per million.

Quantitative Estimation.—A solution of 1 gm. of the acid in water is titrated with decinormal barium hydrate, using phenolphthalein as indicator; 1 c.c. = 0·0075 gm. crystallised tartaric acid.

Uses and Storage.—Pure tartaric acid, free from lead, is used for forensic investigations, and also for the detection of potash compounds and the estimation of oxide of iron. This latter method is described in the "Zeit. f. anal. Chem.," 1888, p. 146. Hampe ("Analyst," 1891, p. 151) uses a pure acid (free from tin in particular) along with nitric acid for the solution of minerals and smelting materials for quantitative analysis.

The double tartrate of potassium and sodium or Rochelle

salt, is used for the preparation of Fehling's solution (see "Copper Sulphate"), and is sold in the form of large, pure crystals.

Solutions of tartaric acid do not keep well, in time developing mould.

Commercial Varieties.—See note under "Tests for Impurities".

TEST PAPERS.—The various test papers are described under the substances from which they derive their names, and also under "Indicators and Test Papers," pp. 140-146.

Ozone paper is described under "Gold Chloride," and below, under "Thallous Nitrate".

TETRAMETHYLPARAPHENYLENEDIAMINE HYDROCHLORIDE.—Formula $N(CH_3)_2 . C_6H_4 . N . (CH_3)_2\ 2HCl$. Crystals soluble in water and in alcohol.

Uses.—Employed as a reagent for ozone, hydrogen peroxide, and oxidases.

THALLIUM CARBONATE.—Thallium Carbonicum Tl_2CO_3. Mol. wt., 468·0. Yellowish crystals. Slightly soluble in water (1 : 20).

Uses.—E. Kurowski has suggested a delicate reagent for carbon bisulphide. This is prepared by boiling thallium carbonate with a solution of acetyl-acetone ($CH_3 . CO . CH_2 . CO . CH_3$) in alcohol. After a time acetyl-acetone thallium is formed ($CH_3 . CO . CTl_2 . CO . CH_3$) and the solution then yields with carbon bisulphide a bulky orange-yellow precipitate. By this means 1 drop of CS_2 in a litre of benzol can be detected. Coloured precipitates are also obtained with other organic sulphur compounds ("Chem. Polski.," 1910, p. 193; Merck's "Annual," 1910, p. 361).

THALLOUS NITRATE.—Thallium nitric. puriss. ($TlNO_3$). Mol. wt., 266·01. Opaque, white rhombic crystals, soluble in 10 parts of water at the ordinary temperature. A saturated, neutral solution is used for the separation of hydrochloric, hydriodic and hydrobromic acids.

Thallium Paper (or ozone paper) is sometimes employed

as an indicator in the estimation of zinc by titration with sodium sulphide, and is also used for the detection of ozone. It is prepared by saturating filter paper with a 10 per cent. solution of thallous hydrate.

Thallous nitrate may be estimated, according to Nietzki, by titration with potassium iodide.

An accurate gravimetric method, depending upon the precipitation of the metal as thallous iodide, is described by Baubigny ("J.C.S.," 1892, A., p. 238).

THIOACETIC ACID.—Acidum thioaceticum. (CH_3COSH). Mol. wt., 76·08. A yellowish liquid, having a pungent smell of acetic acid and hydrogen sulphide. Sp. gr., 1·070. B.p., 92°-97°.

The substance dissolves with difficulty in cold water, and is used in analysis as a substitute for hydrogen sulphide. For use 10 c.c. are dissolved in a slight excess of ammonia and diluted to 30 c.c.; in qualitative tests 1·5 c.c. to 2 c.c. of this solution are used for 1 gm. of the substance. It immediately precipitates the metals of the second group and also arsenites (R. S. Schiff and N. Tarugi, "J.S.C.I.," 1895, p. 509). The acid must be kept in well-stoppered bottles.

Note.—According to E. Merck ("Annual Report," 1895, p. 36) a 30 per cent. solution of the ammonium salt, $CH_3 . C . O(SNH_4)$, is sold under the name of Schiff's reagent,[1] and has a slight smell of ammonium sulphide. This solution has been recommended by Schiff and Tarugi (loc. cit., and "J.C.S.," 1895, A., ii., p. 84) as a substitute for hydrogen sulphide in qualitative analysis, particularly in forensic work for both the qualitative and quantitative determination of arsenic, on account of its freedom from that impurity, and also because by its use a great deal of the trouble involved in employing hydrogen sulphide is avoided. See also a paper on Ammonium dithiocarbonate in "Ber. d. d. pharm. Ges.," 1898, vol. viii., p. 228.

THIOBARBITURIC ACID.—According to G. P. Plaisance ("J. Biol. Chem.," 1917, 207-208) thiobarbituric acid can be employed for distinguishing between the aldoses and the ketoses. On boiling the substance with 12 per cent. hydrochloric acid the ketoses are converted to a greater extent into

[1] This must not be confused with the reagent for aldehydes, i.e., a solution of magenta reduced with SO_2.

hydroxymethylfurfural than are the aldoses, hence on cooling the solution and adding a few drops of a solution of thiobarbituric acid in 12 per cent. hydrochloric acid, an orange-yellow precipitate is formed in the case of the former, whereas with the latter, although the liquid may be yellow, no precipitate is formed.

THIOSINAMINE.—Has been recommended as a reagent for the detection of cadmium and uranium. The reagent is prepared by mixing 95 c.c. of a 5 per cent. solution of thiosinamine and 5 c.c. of sodium hydroxide solution, sp. gr., 1·332, immediately before use. Two or 3 drops of this reagent added to 3 or 4 c.c. of the solution to be tested gives in presence of cadmium or uranium salts a yellow precipitate. There is no reaction with the commoner metals, alkaline earths, or alkalies.

THYMOL.—Thymol puriss. ($C_6H_3(CH_3)(C_3H_7)OH$.) Mol. wt., 150·16. Colourless, lustrous crystals, melting at 50°, boiling at 228°-230° and easily soluble in alcohol and ether. It is sometimes used in Molisch's sugar test in place of α-naphthol; that author also uses it as a test for coniferin ("J.C.S.," 1887, A., p. 692).

Thymol may be employed for the detection of titanium. (V. Lenher and W. G. Crawford, "J.S.C.I.," 1912, 956).

A good general appearance and a correct melting-point will show that the sample is pure.

TIN.—Stannum metallic. pur. (Sn). At. wt., 118·70. A soft metal of white, silvery appearance, melting at 230° C. It dissolves in hot hydrochloric acid, forming the protochloride, and is oxidised to binoxide by concentrated nitric acid.

Tests for Impurities.—The general appearance of the metal is usually a good guide as to its state of purity; the purer it is the more it conforms in appearance to the above description. The chief impurities to be looked for are lead, iron, zinc, copper, arsenic, and antimony. A few grams of the metal are oxidised by evaporating with nitric acid, and the binoxide formed is digested with a little dilute nitric acid, whereby the lead, zinc,

iron, and copper are all dissolved, and may be tested for in the usual way. Arsenic and antimony volatilise on treating the tin with hydrochloric acid, partly as arseniuretted and antimonietted hydrogen, and may be detected by Marsh's test after adding a few drops of platinum bichloride solution.

Quantitative Estimation.—The metal may be estimated gravimetrically as binoxide (SnO_2), or volumetrically, after conversion into protochloride, with standard iodine in alkaline solution (see Sutton's "Vol. Anal.," p. 339).

Uses.—A mixture of tin and hydrochloric acid is used as a reducing agent in analysis and organic synthesis.

Note.—A method of preparing pure tin powder free from oxide is described by Buchner ("J.S.C.I.," 1895, p. 277) as follows: 400 gms. of tin protochloride are dissolved in 6 litres of water, and the solution is poured, with constant stirring, into a mixture of 6 litres of water and 4 litres of caustic soda solution (sp. gr. 1·33) containing 60 gms. of pure cyanide of potassium. Sheets of zinc are then placed in this mixture, and after 5 or 10 minutes the spongy tin is removed and placed in water, and the operation continued till all the tin has been thus precipitated. A fresh quantity of tin salt and soda solution can then be added, and the reaction continued. The spongy metal is then well washed and dried.

Commercial Varieties.—The purest commercial tin (Banca tin) which comes from the East Indies, contains only traces of impurities. English corn tin is said to contain only 0·1 per cent. of impurities, but English block tin, Saxon, and Bohemian tin are not so pure.

According to Fresenius, Banca tin contains 99·90 to 99·96 per cent., whereas crude commercial samples contain often only about 94 per cent. R. Kayser found 1·30 per cent. of mercury in a sample sold as English tin, but really consisting of fused tin refuse ("Zeit. f. angew. Chem.," 1888, No. 7, p. 196). The pure metal for analytical purposes is sold in the form of sticks, precipitated powder and filings.

TIN PROTOCHLORIDE.—Stannum chlorat. cryst. pur. ($SnCl_2, 2H_2O$). Mol. wt., 223·65. Colourless monoclinic crystals, easily soluble in water (1 : 0·37).

Tests for Impurities.—*Alkalies and Earths.*—3 gms. are dissolved in 100 c.c. of water, hydrochloric acid added, and the

tin precipitated with hydrogen sulphide. The filtrate, when evaporated, must leave only traces of residue.

Sulphuric Acid.—The solution (1 : 50) must show no change on acidifying with hydrochloric acid and adding barium chloride.

Ammonia.—No ammonia must be given off on heating with caustic potash.

Arsenic.—2 gms. on boiling with 10 c.c. of pure concentrated hydrochloric acid must give a perfectly clear and colourless solution (see also "Tin Protochloride Solution").

Quantitative Estimation.—For the volumetric estimation with iodine in alkaline solution, see "Tin".

Uses.—The salt, among other uses, is employed for the detection of arsenic and mercury. A standard solution of the salt is used for the estimation of copper and iron (see Sutton's "Vol. Anal.," pp. 128, 181, 210); also as an indicator in the volumetric estimation of sugar by mercurial solutions. The use of the salt as a chemical reagent depends in most cases upon its reducing power.

Commercial Varieties.—Owing to oxidation these varieties often fail to give a clear solution in water, and they are sometimes adulterated with magnesium sulphate. The quality used for commercial purposes nearly always contains a considerable quantity of sulphuric acid.

TIN PERCHLORIDE SOLUTION.—Solutio stanni chlorati. Pale yellow, fuming, refractive liquid. Sp. gr., at least 1·900. The absence of sulphates and hydrogen sulphide is most important when the solution has to be used for the detection of arsenic, as sulphurous acid is first formed, and subsequently hydrogen sulphide. If the latter can be detected by smell, the solution is useless as a reagent ("Pharm. Ztg.," 1896, p. 151), and only preparations which give no reaction with lead paper should be used.

TITANIC ACID.—Titanium dioxide, TiO_2. Mol. wt., 80·1. White powder. Sp. gr., 3·89 to 3·95.

This compound when dissolved in hydrochloric or sulphuric

acid has been shown to give an intense red colour with chromotropic acid (1·8 dioxynaphthalene-3·6 disulphonic acid) and O. Hauser and A. Lewite have shown that the reaction is a general one for all phenols and for the oxy groups generally ("Ber.," 1912, p. 2480, Merck's "Annual," 1911, p. 222, and 1912, p. 452).

TITANIUM TRICHLORIDE.—Formula Ti_2Cl_6. Dark violet scales. Deliquescent and readily soluble in water with the evolution of heat.

Uses.—Titanium trichloride may be employed for the volumetric estimation of nitro and nitroso compounds, methylene blue being used as indicator (H. Salvaterra, "Chem. Zeit.," 1914, 38, pp. 90-91; "J.S.C.I.," 1914, p. 162).

TITANOUS CHLORIDE.—Formula $TiCl_2$. Light brown powder, very hygroscopic and soluble in water with evolution of heat.

Uses.—For the uses of titanous chloride in qualitative analysis, see A. Monnier, "J.S.C.I.," 1915, 152; also 1903, 232-762, 825; 1904, 503; 1905, 1192, and 1907, 1165.

TROPÆOLIN.—Tropæolin 00, orange IV., is the sodium salt of azo-diphenylamine sulphanilic acid, $C_{18}H_{14}N_3O_3SNa$. Orange-yellow plates soluble in water. With alkalies gives a yellow colour and with acids orange-red. According to Boas a saturated alcoholic solution, or a test paper prepared from the same, may be used to detect hydrochloric acid in gastric juice ("Pharm. Ztg.," 1891, p. 392). Regarding the above preparation, and also tropæolin 000, which is also used as an indicator, see Cohn, "Indicators and Test Papers," pp. 168-172, 218.

TURMERIC PAPER.—A yellow paper, coloured a bright sulphur-yellow with acids, reddish-brown with alkalies, and red with boric acid. The turmeric root contains two yellow colours, one soluble in water and the other in alcohol. The former is not sensitive to alkalies, but the one soluble in alcohol is very sensitive. Turmeric paper is therefore rendered far more sensitive if the water-soluble colour is first extracted from

the root by means of a large quantity of water, and the root then extracted with alcohol for the preparation of the tincture in which the papers are dipped. Turmeric paper cannot be used for the carbonates of sodium and potassium, but only for caustic alkalies and earths. It is one of the most sensitive test papers. On its use, see Cohn, "Indicators and Test Papers". The method of procedure in making a test (see Dieterich, "Pharm. Central.," 1887, p. 498) consists in finding its degree of sensitiveness towards caustic potash and ammonia; with the former this ought to be about 180,000 and towards ammonia about 35,000 (see tables under "Indicators").

Note.—In estimating the degree of sensitiveness of test papers, attention may be called to the fact that the strongly diluted solutions of sulphuric and hydrochloric acids, caustic potash and ammonia change within a few days, and must always, on that account, be freshly prepared. In the preparation of these papers, a dilute solution of the pigment must be used, in order to obtain a very sensitive reaction. The delicacy may be increased by previously neutralising the acid, which every paper contains in more or less degree. The paper used for this purpose must be specially manufactured (see Dieterich, loc. cit.).

URANIUM ACETATE.—Uranium aceticum puriss. ($(C_2H_3O_2)_2(UO_2)$, $2H_2O$). Mol. wt., 424·3. Yellow salt, soluble in water.

The salt is tested in the same way as the nitrate, and is used for the same purpose. As it generally contains a little basic salt it is necessary to add a little acetic acid in preparing a solution. Impure qualities are sometimes found containing soda, sulphuric acid, and the proto salt, and are often of poor appearance and imperfectly crystallised.

Test for Salt of Sodium or Other Alkalies.—2 gms. are dissolved in 50 c.c. of water, and precipitated in boiling solution with ammonia and the solution filtered; 15 gms. of dilute sulphuric acid are now added to the filtrate, and, after evaporating and igniting, only traces of residue should remain.

Note.—Most commercial varieties are not pure acetates but the double salt of uranium and sodium.

Uses.—In the volumetric estimation of phosphoric acid (Sutton's "Volumetric Analysis," 17th ed., p. 285).

A 2 per cent. solution of uranium acetate was also proposed as a test for albumen. This has not come into very general use but according to A. Oszacki it is both sensitive and characteristic as it does not precipitate other nitrogenous substances which accompany albumin in the fluids of the body " (Zeit. für innere Med.," 1912, p. 1165; Merck's "Annual," 1912, p. 459).

URANIUM NITRATE.—Uranium nitric. puriss. cryst. ($(NO_3)_2(UO_2)$, $6H_2O$). Mol. wt., 502·32. Fine large greenish-yellow rhombic crystals, easily soluble in water (2 : 1).

Tests for Impurities.—*Sulphuric Acid.*—The aqueous solution (1 : 20) must be clear and show no turbidity with barium chloride on standing for a few minutes.

Earths.—The solution (1 : 20) must remain clear after adding ammonia and excess of ammonium carbonate.

Other Metals.—A solution of 5 gms. in 100 c.c. of water containing 5 c.c. of hydrochloric acid is heated and hydrogen sulphide passed through; no precipitate must appear.

Proto Compound.—1 gm. dissolved in 20 c.c. of water and acidified with 1 c.c. of sulphuric acid must give a permanent red solution after adding 1 drop of $\frac{n}{10}$ permanganate (1 c.c. = 0·0056 gm. Fe), and the solution must remain clear.

Sodium Salt.—Test as under " Uranium Acetate ".

Quantitative Estimation.—Uranium may be estimated by reversing the phosphoric acid method, the acid set free from the salt being converted into acetic acid by decomposition with sodium acetate, and the solution titrated with a standard solution of microcosmic salt (*q.v.*); see Mohr's " Titrirmethode," 6th ed., p. 489.

Uses and Storage.—The salt is used for the preparation of the standard solution for phosphoric acid estimation (see Sutton's " Vol. Anal.," p. 284 *et seq.*). The salts of uranium, whether in dry state or in solution, should be kept in well-stoppered bottles protected from light.

Commercial Varieties.—These often contain sulphates and arsenic, and generally soda or ammonium salts. On their analysis, see J. König, " Rep. f. anal. Chem.," 84, No. 11, p. 161.

WATER, DISTILLED.—Aqua distillata. (H_2O). Mol. wt., 18·02. A clear, neutral liquid, without colour, odour, or taste.

Tests for Impurities.—The neutrality is proved by means of litmus paper, and for the detection of the traces of alkali derived from the glass vessels, see "Iodeosin," p. 155.

Ammonia.—On adding 1 c.c. of Nessler's reagent to 50 c.c. of the water no colour must be produced.

Note.—Regarding the presence of ammonia, see also "Tests for organic substances". In order to free the water from this impurity, sulphuric acid is added before distillation to fix any traces that may be present. Nitrous and nitric acids on the other hand pass over into the distillate on acidifying, and to remove these it is necessary first of all to distil the water by itself (Bisbu, "Rep. d. Chem.-Ztg.," 1891, p. 264). Regarding the preparation of absolutely pure distilled water, see Bremer, "Pharm. Wochenschrift," 1894, p. 97. Hempel and Thiele ("Zeit. f. anorg. Chem.," vol. xi., 1896, No. 2, p. 78) describe an easy method of obtaining it in large quantities, the water being used by them in atomic weight determinations. They found that when prepared on the small scale in glass or tinned copper vessels, minute traces of either hydrochloric acid or ammonia were always present, whereas when distilled on the large scale in a steam boiler fitted with an injector to drive back the condensed steam, the water through continual circulation became self-purifying. The discovery of this method was purely accidental, as the boiler was originally used for evaporating the ordinary water supply.

Nitric Acid.—With diphenylamine, see p. 98.

Hydrochloric Acid.—100 c.c. should give no reaction with silver nitrate.

Sulphuric Acid.—100 c.c. should give no reaction with barium chloride, even on long standing.

Carbonic Acid.—The water should remain clear on mixing with twice its volume of lime water.

Metals, etc.—The water must give no reaction with hydrogen sulphide, ammonium sulphide, ammonia, and ammonium oxalate.

Note.—Siedler ("Rep. d. Chem.-Ztg.," 1895, p. 66) found copper in the ordinary commercial samples; this test ought therefore always to be applied. Distilled water easily dissolves lead and copper especially when it contains carbonic acid.

Volatility.—100 c.c. must leave no residue on evaporation on the water bath.

Organic Substances.—100 c.c., to which 1 c.c. of dilute sulphuric acid (1 : 5) has been added, must not reduce 1 drop of

permanganate solution (1 : 1000), even after boiling for 3 minutes.

Note.—H. Bremer ("Pharm. Wochenschrift," 1894, p. 97) draws attention to the large amount of impurities often present, and gives the following results of four samples titrated with permanganate, according to the method of the German Pharmacopœia :—

	Oxygen Used.	$\frac{n}{100}$ Acid Used to Neutralise.	Ammonia.
A.	0·554 mgms.	3·700 c.c.	large quantity
B.	10·330 „	4·900 „	free
C.	0·080 „	1·100 „	strong traces
D.	0·000 „	0·000 „	free

B gave a residue of 36 mgms. per litre on evaporation, consisting almost entirely of organic matter. Considering the fact that a water which absorbs 2 mgms. of oxygen per litre, would, under ordinary circumstances, be condemned as unfit for drinking purposes, Bremer is right in regarding the limit of 0·7 mgm. oxygen absorbed as being too high. Eschbaum ("Ber. d. pharm. Ges.," Berlin, 1895, Nos. 7 and 8) detected an oxidising substance which decomposed potassium iodide solution in commercial distilled water.

Storage.—As the atmosphere is never free from ammonia, carbonic acid, and particles of dust containing the spores of algæ and other organisms, vessels containing the water ought to be tightly stoppered. On keeping, the water readily absorbs traces of alkali from the glass (see "Iodeosin," p. 155).

XYLIDINE ($C_6H_3(CH_3)_2NH_2$). Mol. wt., 121·14. Commercial xylidine is a mixture of several isomers, but consists chiefly of metaxylidine (b.p., 212°) and paraxylidine (b.p., 215°). Witt, Noelting, and Forel have published an article regarding the composition of the commercial substance in "Chem. Centralblatt," 1889, p. 243 (also see "J.S.C.I.," 1889, p. 274), and, according to them, it contains 25 per cent. paraxylidine. Regarding the separation of the isomers by means of sulphurous anhydride, see E. Börnstein, "Chem.-Ztg.," 1891, p. 632. When mixed with acetic acid it forms a very sensitive test for furfurol, according to Hugo Schiff ("Rep. d. Chem.-Ztg.," 1887, p. 83).

ZINC.—(*a*) **Zinc. metallic. puriss.** (Zn). At. wt., 65·37. A bright, white metal with a slight bluish-grey tint. It is sold in powder, small sticks, or granulated.

Tests for Impurities.—*Arsenic.*—20 gms. of the zinc are placed in a Marsh apparatus of about 200 c.c. capacity, and the evolution of hydrogen sustained by means of dilute sulphuric acid (1 : 3) until the metal is almost all dissolved; no arsenic reaction must take place during this operation, which generally lasts several hours.

Note.—A little platinum bichloride is often added to hasten the process, but Thiele considers this objectionable owing to the risk of traces of arsenic combining with the platinum ("J.S.C.I.," p. 1891, p. 950).

Iron, Lead, Copper, etc.—10 gms. in a small bottle fitted with an india-rubber valve are dissolved in about 60 c.c. of water and 15 c.c. of pure concentrated sulphuric acid. The solution must only contain minute traces, if any, of black, flocculent specks of undissolved lead, etc. When the metal has almost completely dissolved 1 or 2 drops of $\frac{n}{10}$ permanganate are added; a distinct red colour must be produced (1 c.c. = 0·0056 gm. Fe). The quantity taken is therefore free from iron, or only contains very minute traces. In order to ensure accuracy the sulphuric acid by itself should be titrated with permanganate.

Note.—(*a*) If the zinc and sulphuric acid are really chemically pure, they can remain in contact with each other for days together without solution ensuing. The author brings about solution, therefore, in a platinum capsule, and pours out the solution before the last traces have dissolved; he then titrates with permanganate as above. Further, he considers it necessary to state that if more than 20 gms. of zinc are used for the arsenic test, solution is very often retarded. Since zinc is no longer obtained from *electric calamine*, which is very free from arsenic, great difficulty is experienced in removing larger quantities of arsenic in a really satisfactory way.

Note. (*b*).—As a check on the above method, the iron may be determined by dissolving 10 gms. of the zinc in dilute hydrochloric acid, oxidising the iron with nitric acid, and precipitating with excess of ammonia. The brown flocculent precipitate of ferric hydrate is then washed with water containing ammonia, and, after drying and igniting weighed.

Sulphur, Phosphorus, etc.—Gutzeit's method, which depends on the action of the hydrogen evolved by acid, on paper soaked in silver nitrate solution, is used here. See also notes

under "Zinc Dust," and the estimation of carbon and sulphur under "Commercial Varieties".

Quantitative Estimation.—The qualitative tests for iron, arsenic, and lead are generally sufficient when determining the purity, but an accurate method for their quantitative estimation is given in Fresenius' "Quant. Anal.," vol. ii., p. 286. The results of the examination of the "puriss." zinc are given below.

Uses.—The metal is used in forensic work for the detection of arsenic, and in quantitative analysis for the reduction of ferric oxide in solution; further, for the precipitation of copper from its solutions, and for reducing silver chloride.

Commercial Varieties.—Samples are often sold as "puriss.," containing considerable quantities of iron and lead.

Note.—Mylius and Fromm have published a paper on experiments on the preparation of pure zinc (see "J.S.C.I.," 1895, p. 867). According to these authors the purest zinc can be obtained by repeatedly purifying the metal by electrolysis in basic zinc sulphate solution; a metal thus prepared contains at least 99·99 per cent. They consider the purest commercial zinc still contains some lead, cadmium, and iron; 100,000 parts of "puriss." commercial zinc were found to contain these impurities in the following proportion :—

	Maximum.	Minimum.
Iron	36	1·4
Cadmium	111	5
Lead	72	5

Regarding the presence of sulphur and carbon, see a paper by Funk in "J.S.C.I.," 1896, p. 200; "J.C.S.," 1896, A., ii., p. 274. The percentage of carbon is always very small. The estimation of sulphur gave the following results :—

Source.	Quantity Taken in Gms.	Sulphur Mgms.	In One Million Parts.
1. Zinc II from Kahlbaum . . .	22	0·005	0·23
2. ,, ,, ,, . . .	22	0·0048	0·22
3. ,, ,, ,, . . . (repeatedly fused and filtered).	20	—	—
4. Zinc from Trommsdorff . . .	17	0·003	0·18
5. Zinc, "absolutely chem. pure," from Merck	23	—	—
6. Zinc, specially pure, from Kahlbaum	24	—	—
7. Zinc, specially pure, rolled . .	22	0·008	0·36
8. Zinc, electrolytically purified and sublimed	20	0·002	0·10

The methods and apparatus used by Funk are described in detail in the above-mentioned article. The sulphur was detected by the very delicate reaction which para-amido-dimethylaniline and ferric chloride give with hydrogen sulphide (formation of methylene blue).

(*b*) **Zinc, Absolutely free from Arsenic.**—The preparation has a metallic lustre, and is sold both in the granulated form, and in the form of small sticks.

Tests for Impurities.—*Arsenic.*—In exactly the same manner as under "Zinc puriss."

Quantitative Estimation.—No arsenic must be present, and the other impurities are estimated quantitatively, according to Fresenius, "Quant. Anal.," vol. ii., p. 286.

Uses.—It is used for Marsh's test.

Commercial Varieties.—These sometimes fail to pass Marsh's test, in spite of their label, "Free from arsenic".

The electrolytic zinc is now sold in a very pure state, containing as much as 99·9 per cent. The author, on examining a sample of this variety, found a considerable quantity of arsenic present; another sample showed complete absence of this impurity.

(*c*) **Zinc Dust.**—Zinc. metallic. pulv. A fine grey powder, containing about 95 per cent. of zinc.

Tests for Impurities and Quantitative Estimation.—The quality is ascertained by estimating the metallic zinc present, which may be done, according to Fresenius, by dissolving the zinc dust in dilute sulphuric or hydrochloric acid, burning the hydrogen evolved, and weighing the water thus formed. Each equivalent of water equals one equivalent of zinc used.

Drewson's method is generally used in practice (Fresenius, "Quant. Anal.," vol. ii., p. 289). A very simple method, more accurate than the above, is given by Topf ("J.C.S.," 1887, A., pp. 688, 997), and is based on the formation of iodide of zinc through the direct combination of the zinc with iodine, the latter being in excess in neutral solution. The chromic acid method may also be mentioned, and is described by W. Minor in "J.S.C.I.," 1890, p. 1153.

Uses.—Zinc dust is used for reducing purposes, as, for instance, in the estimation of nitric acid, reduction of indigo, etc.

Commercial Varieties.—The percentage of zinc present varies

very considerably. Muspratt ("Techn. Chemie") gives an analysis of a sample yielding only 29 per cent. The other chief constituent is oxide of zinc. W. Minor (loc. cit.) found 86·95 per cent. of zinc, 1·43 of cadmium, and 0·07 of iron. A. Wagner ("J.C.S.," 1882, A., p. 670) found from 0·11 to 0·12 per cent. of sulphur in one sample. Some zinc sticks purchased as chemically pure contained 0·004 per cent. of this impurity. For further analyses, see Muspratt, loc. cit., vol. vii., p. 1242.

Note.—The sulphur can be estimated by passing the gases evolved on dissolving 10 gms. of zinc dust in dilute acid into a solution of a cadmium salt, and weighing the cadmium sulphide formed.

ZINC ACETATE.—Zincum aceticum, $Zn(C_2H_3O_2)_2 + 2H_2O$. Mol. wt., 175·47. White scales soluble in water.

Tests for Impurities.—*Sulphates.*—Barium chloride should give no cloudiness.

Chlorides.—Silver nitrate should not give more than a faint turbidity to a solution acidified with dilute nitric acid.

Iron.—The precipitate produced by ammonium sulphide after addition of ammonia should be nearly white (ZnS).

A solution of potassium sulphocyanide should develop no colour.

Lime.—After adding ammonia and ammonium sulphide in excess, ammonium oxalate should produce no turbidity.

Magnesia.—The foregoing solution, after addition of sodium phosphate, should yield no precipitate even after long standing.

Uses.—Zinc acetate in conjunction with pyridine and chloroform has been suggested by A. Florence ("Jour. de Pharm. Chem.," 1910, p. 160) as a test for urobilin, urobilinogen, and blood (Merck's "Annual," 1910, p. 376).

ZINC CHLORIDE.—Zincum chloratum, pur. ($ZnCl_2$). Mol. wt., 136·29. White, hygroscopic powder or sticks, easily soluble in almost all proportions in water and in alcohol.

Tests for Impurities.—*Solubility.*—The solution of 1 part of the salt in 1 part of water must be clear, or only slightly turbid, and the flocculent precipitate formed by adding

3 parts of alcohol to this solution must immediately dissolve on adding 1 drop of hydrochloric acid.

Note.—It is a well-known fact that the absolutely neutral salt is decomposed on adding water in excess. A precipitate of oxychloride forms on adding water to the clear solution (1 : 1), and the solution will become clear again on adding a little hydrochloric acid. Any sample which does not show this turbidity on treating as above contains free acid.

Sulphuric Acid, Foreign Metals, etc.—The aqueous solution (1 : 10) must not become turbid on adding hydrochloric acid and barium nitrate, nor be coloured by hydrogen sulphide water. A clear solution must be formed on dissolving 1 gm. in 10 c.c. of water and 10 c.c. of ammonia, and the addition of hydrogen sulphide water must produce a pure white precipitate, the filtrate from which must leave no residue on evaporation and ignition.

Note.—The above test is taken from the third German Pharmacopœia.

Quantitative Estimation.—For the pure salt the above test affords a sufficient examination for purity, but in the case of the crude commercial salt used in the dyeing industry as a dehydrating agent, the specific gravity of its solution must be taken, and the percentage of $ZnCl_2$ calculated therefrom (see Böckmann, "Chem.-techn. Untersuch.," 3rd ed., vol. ii., p. 72).

Uses and Storage.—A solution of 1 gm. of the salt in 30 gms. of hydrochloric acid and 30 c.c. of water is used by Jorissen as a reagent for the recognition of certain alkaloids.

According to Cross and Bevan ("Chem. News," vol. lxiii., p. 66) a solution of zinc chloride in twice its weight of hydrochloric acid forms a good solvent for cellulose. In organic synthesis it is used for dehydrating purposes. Owing to its highly hygroscopic nature, bottles containing the salt must have well-fitting stoppers.

Commercial Varieties.—Crude zinc chloride may be obtained in the form of grey lumps which readily absorb moisture. The pure quality has often been found to contain large quantities of sulphate.

ZINC IODIDE.—Zincum iodatum (ZnI_2). Mol. wt., 319·31. Whitish, odourless powder, crystallises in regular octahedrons,

as easily soluble in water and alcohol as zinc chloride. It is tested in the same way as the chloride, and, as it is of equally hygroscopic nature, it must be kept in tightly stoppered bottles. It is used for the preparation of potassio-zinc iodide solution, described on p. 264; also as a group reagent for the alkaloids, and for the preparation of the zinc iodide and starch solution, regarding which, see Cohn, "Indicators and Test Papers," p. 172. The latter is a colourless and slightly opaque liquid, which must be kept in the dark, and which, when diluted with 50 times its volume of water, must not show a blue colour on acidifying with dilute sulphuric acid.

ZINC SULPHATE. — Zincum sulphuric. puriss. ($ZnSO_4$, $7H_2O$). Mol. wt., 287·54. Perfectly colourless rhombic crystals, easily soluble in water ($ZnSO_4$, 1 : 2).

Tests for Impurities.—*Solubility.*—The aqueous solution (1 : 10) must be clear.

Iron.—The solution (1 : 20) must give no reaction with potassium thiocyanate.

Note.—A zinc sulphate, absolutely free from iron, may be obtained as follows: 100 parts of crude arsenic-free sulphuric acid are diluted with 300 parts distilled water, and 70 parts of ordinary commercial zinc are added to the solution while still hot. The mixture is allowed to stand, with frequent stirring, for 2 days, and 25 parts of chlorine water are then added. After again stirring well, the solution is allowed to settle for half an hour, after which 1 part of caustic soda solution is added. When the solution has stood for another half-hour, with frequent stirring, it is filtered and the salt crystallised out ("Pharm. Ztg.," 1894, 39, p. 432).

Other Metals, etc.—As under "Zinc Chloride," p. 347.

Note.—A special test may be made for manganese by heating with peroxide of lead and nitric acid.

Chlorides.—The aqueous solution (1 : 20) must give no reaction with silver nitrate.

Arsenic.—2 gms. in Marsh's apparatus (see under "Sulphuric Acid," p. 323).

Nitrates.—On colouring a few c.c. of the solution (1 : 10) with a drop of indigo solution diluted with twice its volume of water, the blue colour must remain after the addition of a few c.c. concentrated sulphuric acid.

Uses.—In addition to other uses, zinc sulphate may be employed in detecting uric acid in blood, white basic zinc urate being formed (Ganassi, "Rev. Pharm. de Flandres," 1909, p. 361, Merck's "Annual," 1910, p. 376.

Commercial Varieties.—The commercial zinc sulphate is often very impure, containing magnesium sulphate, nitrates, arsenic, iron, and manganese; in spite of the presence of considerable quantities of iron it sometimes has a fine white appearance. A reddish variety, obtained as a by-product in the smelting of manganiferous ores, and often containing several per cent. of manganese, may be bought from the works.

APPENDIX.

1. PREPARATION OF THE ORDINARY REAGENTS.[1]

Acetic Acid.—See p. 3.

Ammonia.—Ammonia of 0·925 sp. gr. is diluted with 1 part of water, by which means a solution of 0·96 sp. gr. and containing 10 per cent. of NH_3 is obtained.

Ammonium Carbonate.—1 part dissolved in a mixture of 3 parts of water and 1 part of ammonia of sp. gr. 0·96.

Ammonium Chloride.—1 part of salt in 9 parts of water.

Ammonium Citrate.—See p. 27.

Ammonium Oxalate.—1 part in 19 parts of water.

Ammonium Sulphide.—See p. 36.

Aniline Colours.—See "Fuchsine Solution," etc., p. 112.

Arsenious Acid, decinormal.—See p. 42.

Azolitmin, Tincture of.—See p. 43.

Barium Acetate.—1 part in 19 parts of water.

Barium Chloride.—1 part in 20 parts of water.

[1] Dünnenberger in a pamphlet entitled "Chemische Reagentien und Reactionen" (Zurich, "Orell Füssli," 1894) describes in detail the methods of preparing the various reagents named after their authors, e.g. Dragendorff's reagent, Ehrlich's reagent, etc. Reagents for microscopical work are described in "Tabellen zum Gebrauche bei mikroskopischen Arbeiten," by Behrens, published in a second edition by Bruhn, Brunswick, 1892. A work containing over 400 special reagents used both in chemical analysis and bacteriology and arranged alphabetically has been published by the authors, Ferdinand Jean and G. Mercier, and is entitled, "Répertoire des Réactifs spéciaux, généralement désignés sous leurs noms d'auteurs" ("Imprimerie," Edmond Rousset, Paris, 1896). Several of these reagents have also been described in the French Edition of the present work, entitled "Essais de Pureté des Réactifs chimiques," par C. Krauch, Dr.Sc., Edition Française, annotée par Julien Delaite, Préface par L. L. de Koninck, Dr.Sc. This edition is published by Marcel, Nierstrasz, Liège.

Barium Hydrate (Baryta water).—1 part in 19 parts of water.

Barium Nitrate.—1 part in 19 parts of water.

Bleaching Powder Solution.—This solution must be freshly made each time, and is prepared by grinding 1 part of the powder in a mortar with 9 parts of water, and filtering off the insoluble.

Borax Solution, decinormal.—See p. 294.

Bromine Water.—A saturated aqueous solution. See also p. 58.

Calcium Chloride.—1 part of the crystallised salt in 9 parts of water.

Calcium Sulphate.—A saturated aqueous solution.

Carmine Solutions (various).—See pp. 72-76.

Chlorine Water.—A saturated solution, of a yellowish-green colour.

Cochineal, Tincture of.—See p. 74.

Cuprammonium Solution.—See p. 93.

Cuprous Chloride, for gas analysis.—See p. 90.

Diphenylamine Solution.—See p. 98.

Dobbin's Reagent.—See p. 299.

Fehling's Solution.—See p. 108.

Ferric Chloride.—1 part in 19 parts of water.

Ferrous Sulphate.—1 part in 8 parts of water and 1 part of dilute sulphuric acid.

Ferrous Tartrate, for the absorption of oxygen, is prepared as follows :—

Dissolve (*a*) 40 gms. cryst. ferrous sulphate in 100 c.c. of water.
,, (*b*) 30 ,, Rochelle salt ,, ,,
,, (*c*) 60 ,, caustic potash ,, ,,

Mix 1 volume of (*a*) with 5 volumes of (*b*), and add to this mixture 1 volume of (*c*). A solution thus prepared readily absorbs oxygen.

Fröhde's Reagent.—See p. 198.

Fuchsine, Methylene Blue, and other solutions for the detection of the tubercle bacillus in sputum (Hueppe, "Chem.-Ztg.," 1890, No. 101) :—

1. The distilled water used for the preparation of these solutions should be sterilised by boiling, or by steam.

2. Absolute alcohol, and the 90 per cent. alcohol of the Pharmacopœia are used for the preparation of concentrated staining solutions. A 60 per cent. alcohol is also used for some purposes.

3. Carbolic acid, 5 per cent. solution.

4. Nitric, hydrochloric, and sulphuric acids, diluted with water in the proportion of 1 : 10, are used for decolorising.

5. A solution of 1 gm. of fuchsine in 10 c.c. of absolute alcohol and 90 c.c. of 5 per cent. carbolic acid is used for staining the tubercle bacillus. The fuchsine is dissolved in the alcohol, the carbolic acid added, and the solution filtered, if necessary. Prepared in this way, the solution will keep for months.

6. The following solutions are used for contrast and ground staining :—

(*a*) *Aqueous Methylene Blue.*—A concentrated aqueous solution of the colour, which requires to be often renewed and filtered, or a concentrated alcoholic solution, is added in sufficient quantity to a small quantity of water to impart a dark blue colour.

(*b*) A concentrated alcoholic solution of yellow fluorescein, to which methylene blue has been added till saturated.

(*c*) *Picric Acid-aniline Oil.*—A saturated solution of picric acid in aniline oil is obtained by grinding them together until no more picric acid dissolves. After settling, the solution is decanted, and for use 2 or 3 drops are added to some pure aniline oil.

For the detection of micro-organisms in water, both fuchsine and methylene blue in solution are used ("Pharm. Ztg.," 1889, p. 37). For this purpose a saturated alcoholic solution is first prepared, and then diluted until a layer of 3 c.m. appears just transparent. Regarding other solutions and reagents for the same test, also gelatine meat infusion, see "Pharm. Ztg.," loc. cit., and also note, p. 351.

Guaiacum, Tincture of.—See p. 118.

Hæmatoxyline Solution.—See p. 118.

Hydrochloric Acid, dilute.—1 part of pure acid (sp. gr. 1·19) diluted with 3 parts of water.

Hydrochloric Acid, normal.—See p. 129.

Hydrogen Sulphide Water.—A thoroughly saturated solution in water.—See p. 329.

Indigo-Carmine Solution.—See p. 148.

Indigo Solution.—See p. 148.

Iodine Solution (solution of iodine in potassium iodide).—A few crystals of potassium iodide are dissolved in water and iodine added until the solution is brown (R. Otto).

Iodine Solution, decinormal.—See p. 150.

Kieffer's Reagent.—See p. 94.

Lacmoid Indicator.—See p. 165.

Lead Acetate.—1 part dissolved in 9 parts of water.

Lime Water.—1 part of quicklime is slaked, then shaken up with about 50 parts of water and allowed to settle for several hours. The supernatant liquid is then drawn off, and the residue again shaken with 50 c.c. of water, filtered, and the filtrate added to the other solution.

Litmus, Tincture of.—See p. 177.

Magnesia, Mixture.—See p. 182.

Magnesium Sulphate.—1 part in 9 parts of water.

Manganese Metaphosphate.—See p. 227.

Mayer's Solution.—See p. 191.

Mercuric Chloride.—1 part in 19 parts of water.

Mercuric Nitrate Solution, for urea estimation.—See p. 190.

Methylene Blue Solution.—See pp. 194, 351.

Millon's Reagent.—See p. 190.

Molybdenum Solution.—See p. 197.

Nessler's Reagent.—See p. 189.

Nitric Acid, dilute.—1 part of the acid, sp. gr. 1·2, is diluted with 2 parts of water.

Nitric Acid, normal.—See p. 208.

Normal Acid Solutions.—See p. 257.

Normal Alkaline Solutions.—See p. 257.

Nylander's Reagent.—See p. 57.

Oxalic Acid, normal.—See p. 215.

Palladium Protochloride Solution.—See p. 217.

Phenol Phthalein.—1 part is dissolved in 100 parts of dilute alcohol.

Phloroglucin-Vanilin.—See p. 223.

Phospho-Antimonic Acid.—To 3 volumes of a fairly con-

centrated aqueous solution of sodium phosphate is added 1 volume of antimony terchloride (R. Otto).

Phospho-Molybdic Acid.—The pure acid dissolved in water. Uses, see p. 223.

Phospho-Tungstic Acid.—To a solution of pure sodium tungstate is added a little pure phosphoric acid (R. Otto), or a solution of the acid in water may be prepared. Uses, see p. 224.

Picro-Carmine.—See p. 230.

Platinum Chloride.—1 part in 19 parts of water. A concentrated solution is also prepared to equal 5 per cent. of metallic platinum.

Potassio-Bismuth Iodide.—This solution is prepared with bismuth iodide in the same way as the following cadmium iodide. Uses, see p. 264.

Potassio-Cadmium Iodide.—Cadmium iodide is dissolved in a hot, concentrated aqueous solution of potassium iodide, and the same volume of the latter as was required for solution, added (R. Otto). Uses, see p. 264.

Potassio-Mercuric Iodide (Meyer's Reagent).—1·344 gms. of mercuric chloride is dissolved in 60 c.c. of water, and potassium iodide added to redissolve the precipitate at first formed. 5 gms. of the solution being then made up to 100 c.c. Uses, see pp. 191, 264.

Potassio-Zinc Iodide.—Prepared from zinc iodide in the same way as the cadmium compound. Uses, see p. 264.

Potassium Bichromate.—1 part in 19 parts of water.

Potassium Carbonate.—1 part in 4 parts of water.

Potassium Chromate, neutral.—1 part in 19 parts of water.

Potassium Ferricyanide.—1 part in 19 parts of water.

Potassium Ferrocyanide.—1 part in 19 parts of water.

Potassium Hydrate.—Aqueous solution, 1 : 6.

Potassium Hydrate, normal.—See p. 257.

Potassium Iodide.—1 part in 9 parts of water.

Potassium Permanganate, decinormal.—See p. 270.

Potassium Permanganate Solution.—1 part in 1000 parts of water.

Potassium Sulphide.—See p. 274.

Potassium Sulphocyanide.—1 part in 19 parts of water.

Pyrogallic Solution, for gas analysis.—See p. 277.

Silver Nitrate, decinormal.—See p. 283.

Sodio-Cobaltic Nitrite.—See pp. 85, 310.

Sodio-Palladium Protochloride.—See p. 217.

Sodium Carbonate.—1 part in 4 parts of water.

Sodium Chloride, decinormal.—See p. 302.

Sodium Hydrate.—Aqueous solution, 1 : 6.

Sodium Hydrate, normal.—See p. 305.

Sodium Hypobromite.—See p. 61.

Sodium Nitroprusside.—See p. 313.

Sodium Phosphate.—1 part in 9 parts of water.

Sodium Sulphide.—See p. 316.

Sodium Thiosulphate, decinormal.—See p. 317.

Starch Solution.—See p. 320.

Sulphuric Acid, dilute.—A mixture of 5 parts of water with 1 part of the pure acid.

Sulphuric Acid, normal.—See p. 326.

Tannic Acid.—1 part in 19 parts of water. To be freshly prepared each time.

Thoulet's Solution.—See p. 191.

Stannous Chloride Solution.—For the detection of arsenic by Bettendorf's method ("Zeits. f. anal. Chem.," 1893, p. 604). The reagent must be free from sulphates, and must be thoroughly saturated with hydrochloric acid. See p. 127.

Zinc Iodide and Starch Solution.—See p. 349.

2. PREPARATION OF REAGENT SOLUTIONS ACCORDING TO BLOCHMANN.[1]—As the degree of concentration to be observed in preparing the above solutions is quite arbitrary, Blochmann[2] has proposed to adopt stoichiometrical proportions, and arranges them in the following order:—

Double Normal.—The acid and alkaline solutions and the ammonium and sodium salts with the exception of disodium phosphate.

Half-Normal.—The solutions of the precious metals (including mercuric chloride) and barium nitrate.

[1] J. König, "Untersuchung landwirthschaftlich und gewerblich wichtiger Stoffe," Berlin, 1891.

[2] R. Blochmann, "Erste Anleitung zur qualitativen chemischen Analyse," Königsberg, 1890.

Normal.—All the other reagents.

In adopting these strengths, equal volumes of the various reagents are equivalent, or, at least, correspond to each other in simple proportions. The solutions thus prepared are easier to manipulate, and waste of reagent is prevented. From the quantity of the reagent used it is also a simple matter to estimate roughly the amount of the substance to be tested for. Reagents which do not dissolve in water in stoichiometrical proportions at the ordinary temperature are employed in the form of saturated solutions, the word "water" being added, as, for example, lime water, bromine water, etc. Oxidising and reducing agents are so prepared that 1 litre of the solution is capable of giving up or absorbing 8 gms. of oxygen.

Concentrated acid solutions are either free from water (concentrated sulphuric acid), or exist as saturated solutions (concentrated hydrochloric acid). In the case of nitric acid a mixture of equal parts of water and the concentrated acid will suffice. The following table gives the weights to be used of the more important reagents:—

1. Concentrated Acids.

	Sp. Gr.	Per Cent. by Weight.	
Hydrochloric acid . .	1·160	31·8	about 10 times normal
Nitric Acid . . .	1·305	48·1	„ 10 „ „
Sulphuric Acid . .	1·840	96·0	„ 20 „ „

2. Normal Solutions.

(*a*) Double Normal $\frac{2N}{1}$.

(One litre contains twice the hydrogen equivalent in grams of the substance.)

Acids:—

	Sp. Gr.	Per Cent. by Weight.	1 Litre Contains	
Hydrochloric acid . .	1·034	7·1	$2HCl$ . . . =	73 gms.
Nitric acid . . .	1·070	11·8	$2HNO_3$ . . =	126 „
Sulphuric acid . . .	1·063	9·2	$2\frac{H_2SO_4}{2}$ . . =	98 „
Acetic acid . . .	1·017	11·8	$2C_2H_4O_2$ . . =	120 „
Oxalic acid . . .	1·042	12·3	$2\frac{C_2H_2O_4 2H_2O}{2}$. =	126 „
Tartaric acid . . .	1·066	14·1	$2\frac{C_4H_6O_6}{2}$ . . =	150 „

Alkalies :—

	Sp. Gr.	Per Cent. by Weight.	1 Litre Contains	
Caustic potash	1·085	10·3	$2KHO$	= 112 gms.
Caustic soda	1·084	7·4	$2NaOH$	= 80 ,,
Ammonia	0·985	3·5	$2NH_3$	= 34 ,,

Salts :—

Ammonium sulphide[1]	1·000	6·8	$2\frac{(NH_4)_2S}{2}$	= 68 ,,
Ammonium chloride	1·032	10·4	$2NH_4Cl$	= 107 ,,
Ammonium carbonate[2]	1·025	9·4	$2\frac{(NH_4)_2CO_3}{2}$	= 96 ,,
Sodium carbonate	1·105	9·6	$2\frac{Na_2CO_3}{2}$	= 106 ,,
Sodium acetate	1·080	25·2	$2NaC_2H_3O_2, 3H_2O$	= 272 ,,

(*b*) Normal $\frac{N}{1}$.

(One litre contains the hydrogen equivalent in grams of the substance.)

	Sp. Gr.	Per Cent. by Weight.	1 Litre Contains	
Disodium phosphate[3]	1·048	11·4	$\frac{Na_2HPO_4, 12H_2O}{3}$	= 119·2 gms.
Magnesium sulphate	1·059	11·6	$\frac{MgSO_4, 7H_2O}{2}$	= 123·0 ,,
Barium chloride	1·088	11·2	$\frac{BaCl_2, 2H_2O}{2}$	= 122·0 ,,
Calcium chloride	1·043	10·5	$\frac{CaCl_2, 6H_2O}{2}$	= 109·5 ,,
Ferric chloride	1·038	5·2	$\frac{Fe_2Cl_6}{6}$	= 54·2 ,,
Lead acetate	1·118	16·9	$\frac{Pb(C_2H_3O_2)_2, 3H_2O}{2}$	= 189·5 ,,
Copper sulphate	1·075	11·6	$\frac{CuSO_4, 5H_2O}{2}$	= 124·8 ,,
Potassium iodide	1·120	14·8	KI	= 166·0 ,,
Potassium chromate	1·075	9·0	$\frac{K_2CrO_4}{2}$	= 97·2 ,,
Potassium ferrocyanide	1·060	10·0	$\frac{K_4FeCy_6, 3H_2O}{4}$	= 105·5 ,,

[1] Half a litre of ammonia is saturated with hydrogen sulphide, and then mixed with half a litre of ammonia, sp. gr. 0·985. The solution soon turns yellow owing to the formation of polysulphide.

[2] 80 gms. of commercial ammonium carbonate in a third of a litre of ammonia, sp. gr. 0·985, are diluted with water to a litre.

[3] The hydrogen equivalent calculated to phosphoric acid.

(*c*) Semi-Normal $\frac{N}{2}$.

(One litre contains half the hydrogen equivalent in grams of the substance.)

	Per Cent. by Weight		1 Litre Contains
Platinic chloride	9·5	$\frac{1}{2}\frac{PtCl_4, 2HCl}{2}$	= 102·3 gms.[1]
Silver nitrate	8·0	$\frac{1}{2}AgNO_3$	= 85·0 ,, [2]
Mercuric chloride	6·4	$\frac{1}{2}\frac{HgCl_2}{2}$	= 67·8 ,,
Barium nitrate	6·2	$\frac{1}{2}\frac{Ba(NO_3)_2}{2}$	= 65·2 ,,

3. Oxidising and Reducing Agents.

(One litre of solution is equivalent to $\frac{1}{2}O$, or 8 grams of oxygen.)

	Per Cent. by Weight.		1 Litre Contains
Potassium bichromate	4·7	$\frac{K_2Cr_2O_7}{6}$	= 49·2 gms.
Sodium hypochlorite	3.7 [3]	$\frac{NaClO}{2}$	= 37·2 ,,
Potassium nitrite	4·2	$\frac{KNO_2}{2}$	= 42·5 ,,
Tin protochloride	10·5	$\frac{SnCl_2, 2H_2O}{2}$	= 112·5 ,,

4. Saturated Solutions.

	Per Cent. by Weight.		
Hydrogen sulphide water	about 0·48, H_2S	about	$\frac{1}{4}$ normal
Baryta water	,, 3·20, $Ba(OH_2)$	,,	$\frac{2}{5}$,,
Lime water	,, 0·70, $Ca(OH)_2$	,,	$\frac{1}{2\frac{1}{2}}$,,
Calcium sulphate water	,, 0·20, $CaSO_4$	,,	$\frac{1}{3\frac{1}{3}}$,,
Bromine water	,, 3·20, Br	,,	$\frac{2}{5}$,,
Iodine solution [4]	,, 4·50, I	,,	$\frac{2}{3}$,,

[1] Equal to about 50 gms. platinum.

[2] Equal to about 50 gms. silver.

[3] Equivalent to about four times the quantity of bleaching powder containing 25 per cent. available chlorine.

[4] On dissolving 50 gms. of iodine and 75 gms. of potassium iodide in about 50 c.c. of water and diluting to a litre, a solution is obtained of sp. gr. 1·10 and containing 4·5 per cent. by weight of iodine. It is equivalent to saturated bromine water.

APPENDIX.

1918.

International Atomic Weights.

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	88·7
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

INDEX.

Acetic Acid, 3.
specific gravity table, 4.
use of, in Goldenberg's method for the estimation of tartaric acid, 5.
use of, in Adamkiewicz's test for albumen, 5.
Acetic Anhydride, 5.
use of, in the estimation of lanoline, 6.
use of, in the acetine method for estimation of glycerine, 6.
use of, in the Liebermann-Storch test for rosin, 6.
reagent, Hirschsohn's, 6.
Acetone, 6.
quantitative estimation of, 7, 17.
Alcohol (spirits of wine and methylated spirit), 15.
Alcohol, Amyl, 8.
use of, in milk testing, 9.
Alcohol, Ethyl, 9.
Glasenapp's modification of Röse's method for fusel oil in, 10.
Bornträger's test for acrolein and fusel oil in, 10.
various tests for aldehyde in, 10.
Léon Crismer's method for the estimation of water in, 12.
for the estimation of boric acid, 13.
purification of, 14.
specific gravity table, 14.
detection of, 95.
Alcohol, Methyl, 16.
use of, in the detection of salicylic acid, 17.
use of, in the estimation of boric acid, 17.
specification for the commercial, 17.
Aldehyde, 18.
tests for, 10, 101, 193, 282.
Alizarinmonosulphonic Acid, 18.
Alkaloid Reagents, 191, 264, 348, 349.
Alkanet Tincture, 19.
Alum Carmine, 73.
Alumina, Moist, 19.
Aluminium, 19.
use of, in the estimation of nitric acid, 22.
as a reducing agent, 22.
amalgam, 22.
presence of sodium in, 23.
Ammonia, Anhydrous, 32.
Ammonia Carmine, 73.
Ammonia-Cupric Sulphate, 23.
Ammonia-Silver Nitrate, 24.
Ammonium Acetate, 24.
Ammonium Carbonate, 24.
estimation of commercial, 25.
Ammonium Chloride, 26.
as a standard for the estimation of acids, etc., 27.
Ammonium Citrate, 27.
Ammonium Fluoride, 28.
Ammonium Hydrate, 29.
Ost's test for empyreumatic substances in, 29.
Bernbeck's test for tar products in, 29.
specific gravity table, 32.
Ammonium Molybdate, 33.
detection of phosphoric acid in, 33.
Ammonium Nitrate, 34.
Ammonium Oxalate, 34.
as a standard for permanganate solutions, 35.
Ammonium Phosphate, 35.
Ammonium Picrocarminate, 73, 230.
Ammonium Sulphate, 35.
use of, in the separation of albuminoids, 36.
Ammonium Sulphide Solution, 36.
as a test for hydrocyanic acid, 37.
preparation of, 37.
Ammonium Sulphocyanide, 38.
as a test for iron, etc., 39.
uses of, in volumetric analysis 39.
Amylum, 320.
Amylum, soluble, 320.

Aniline, 40.
use of, in the estimation of nitrous acid, 40.
as a test for furfurol, amyl alcohol, and aldehyde, 12, 40.
colour reactions of, with essential oils, 40.
as a test for chloroform, chloral, etc., 40.
as a test for woody fibre, 40.
use of, in microscopy, 40.
commercial varieties of, 41.
Aniline Colours and Staining Solutions, 73, 87, 108, 112, 140, 155, 165, 194, 196, 229, 230, 233, 281, 339, 352, 353.
Aniline Salts, 40.
Appendix, 351.
Arsenic, Marsh's test described, 125, 297, 323, 344.
other tests for, 125-128, 338.
Arsenious Anhydride, 41.
detection of sulphide in, 42.
preparation of pure, from commercial, 42.
Atomic Weights of the Elements, 360.
Azolitmin, 43.
paper, 44.
tincture, 44.

Barium Acetate, 44.
Barium Carbonate, 45.
native (witherite), 46.
Barium Chloride, 46.
preparation of absolutely pure, 47.
Barium Dioxide, 47.
Barium Hydrate, 48.
preparation of absolutely pure, 49.
analysis of a commercial, 49.
Barium Nitrate, 49.
preparation of absolutely pure, 50.
Barium Oxalate, 50.
preparation of pure, 50.
Barium Peroxide, 47, 139.
Barium Sulphide, 50.
use of, in the preparation of pure hydrogen sulphide, 51.
Benzene (Benzol), 51.
tests for thiophene in, 51.
test for carbon bisulphide in, 51.
Benzidene, 53.
Benzil Dioxime, 97.
Benzoic Acid, 53.
Benzoyl Peroxide, 55.
Bismuth, 55.
analyses of, 55, 56.
Bismuth Hydrate, 57.
Bismuth Protonitrate, 56.
use of, in the preparation of Nylander's reagent, 57.
Bleaching Powder, 57.
in cubes, 58.
use of, for the detection of aniline, 58.
use of, in the preparation of oxygen, 58.
solution, preparation of, 352.
Boas' Reagent, 329.
Bone Black, 77.
Borax (Sodium Borate), 2.4.
Borax Carmine, 73.
Böttger's Ozone Paper, 117.
Bromchloroform, 61.
Bromine, 58.
quantitative estimation of chlorine in, 59.
gaseous, use of, in analysis, 61.
Bromine Water, preparation of, 61, 352.
Brucine, 61.
use of, in the estimation of nitric acid, 62.

Cadmium, 62.
for testing gold, 63.
Cadmium Borotungstate Solution, 63.
Cadmium Iodide, 63.
Calcined Magnesia, 183.
Calcium Carbonate, 63.
test for alkalies in, 64.
Calcium Chloride, 64.
varieties of, 65.
Calcium Orthoplumbate, 172.
Calcium Oxide, from marble, 65.
prepared from calcium nitrate, 66.
distinction between commercial varieties of, 66.
from Iceland spar, 66, 67.
Calcium Phosphate (dicalcium phosphate), 67.
preparation of, 68.
Calcium Superphosphate (diacid), 68.
preparation of, 68.
Calcium Phosphate, neutral (tricalcium phosphate), 68.
preparation of, 68.
Calcium Sulphate, 69.
solution, as a test for barium, strontium, and oxalic acid, 69.
Calcium Sulphide, 69.
preparation of, 70.
Caliche, 310.
Cane Sugar, 321.
Caramel, standard solution of, 77.

Carbazol, 70.
Carbol Fuchsine, preparation of, 352.
Carbolic Acid (Phenol), 219.
Carbon Dioxide, 70.
Carbon Disulphide, 71.
explosions of, 71.
Carbon Tetrachloride, 72.
Carbo Sanguinis, 77.
Carmine, 72.
adulteration of, 72.
colorimetric estimation of, 73, 76.
staining solutions, 73, 74, 230.
analyses of genuine samples of, 75.
Carmine Paper, red, 74, 142.
blue, 142.
Carminic Acid, 75.
colorimetric estimation of, 73, 76.
Caustic Alkali, detection and estimation of, in alkaline carbonates, 255, 299, 307.
Cellulose, Cuprammonium Hydroxide, a solvent for, 93.
Charcoal, Animal, 77.
determination of decolourising power of, 77.
tests for sugar and calcium sulphide in, 78.
(bone black and blood charcoal), 78.
Chloral Hydrate, 79.
Chloric Acid, 79.
Chlorine, 80.
Chlorine Water, 80.
prepared from liquid chlorine, 80.
Chloroform, 81.
purification of, 82.
varieties of, 82.
Chrome, orange, 172.
red, 172.
yellow, 172.
Chromic Anhydride, 82.
various uses of, in analysis, 84.
for microscopical work, 84.
Citrate Solutions for phosphoric acid estimation, 85.
Citric Acid, 84.
Cobalt and Nickel, methods for the separation of, 86.
Cobalt Acetate, 86.
Cobalt Nitrate, 86.
Cobalt Sodium Nitrite, 85.
Cochineal (indicator and paper), 73, 87.
determination of colouring capacity of, 73, 76.
Congo Red, 87.
paper, 87.
Copper, 88.
analyses of commercial, 88.
preparation of pure metallic, 88.
preparation of electrolytic, 89.
Copper Ammonium Chloride, 89.
Copper Hydrate, 93.
Copper Oxide, powder, 91.
wire and granulated, 93.
Copper Potassium Chloride, preparation of, 89.
Copper Solutions for the estimation of carbon in iron, 89, 90.
Copper Sulphate, 93.
use of, in the precipitation of iodine, 94.
anhydrous, 94.
Copperas (commercial iron sulphate), 162.
Cream of Tartar (potassium bitartrate), 238.
Cupferron, 95.
Cuprammonium Hydroxide, 93.
Cupric Chloride, 90.
anhydrous, 90.
Cuprus Chloride, 90.
solutions for gas analysis, 91.

1 = 2 Diamino anthraquinone = 3 = sulphonic acid, 99.
Diazobenzene Sulphonic Acid, 95.
Diazoresorcin, 165, 166.
Dicyandiamidine Sulphate, 96.
Diiodofluorescein, 155.
Digitonin, 96.
Dimethylamido = benzaldehyde, 96.
Dimethylaniline, 96.
Dimethylglyoxime, 97.
Dimethylsulphate, 98.
Dimethyl Para=phenylene=diamine, 98.
Diphenylamine, 98.
solution, 98.
test as applied to sulphuric acid, 98, 322.
Diphenylbenzidine, 99.
Diphenyl Carbazide, 99.
Dobbin's Reagent, preparation of, 299.

Ehrlich's Test, 96.
Erythrosin (Iodeosin), 155.
Ether, tests for alcohol in, 102.
precautions to be taken in working with, 103.
formation of hydrogen peroxide in, 103.
purification of, 104.
various tests for water in, 105.

Ether, Ethyl, 100.
free from water, distilled over sodium, 105.
Ether Petroleum 106.
test for benzol in, 106.
presence of "hydrocarbon" in, 106.
purification of, 52.
Eugenol (eugenic acid), 108.

Fehling's Solution, and other copper solutions for sugar estimation, 108.
precautions in making alkaline tartrate for, 109.
Fluorescein, 112.
Fluorescein = methylene Blue, preparation of, 353.
Formaldehyde, 110.
Formalin and Formal, 112.
Fothergill Hydrobromic Acid, 123.
Fröhde's Reagent, 198.
Fuchsine, 112.
acid, 113.
carbol, 352.
Furfurol, 114.

Gallein, 114.
Gallic Acid, 114.
Glass, presence of arsenic in, 159.
solubility of, in various solutions, 125, 133.
Glycerin, 115.
Glycerol, 115.
Glucose, 117, 320.
Gold Chloride, 116.
Gold Salts, analysis of, 116.
Grape-Sugar, 117, 320.
Guaiacum, tincture of, 118.
tincture of, as a test for blood, 118.
tincture of, as a test for ozone, 118.
Günzberg's Reagent, 223.
Gypsum, 69.

Hæmatein, 119.
ammonium salt of, 119.
Hæmatoxyline, 118.
paper, 119.
staining solution, 119.
Hanus Solution, 155.
Hoffmann's Reagent, 191.
Hubl Solution, 154.
Hydrazine Sulphate, 120.
Hydriodic Acid, 120.
specific gravity table, 121.
use of, in lead sulphate analysis, 122.
Hydrobromic Acid, 122.
specific gravity table, 123.
use of, in the estimation of sulphur, 123.
Fothergill, 123.
Hydrochloric Acid, 123.
arsenic free, 125.
presence of organic chlorides, tin, etc., in, 129, 132.
normal solution of, 129.
specific gravity tables, 130, 131.
commercial, 132.
commercial, estimation of arsenic in, 132.
Hydrofluoric Acid, 133.
estimation of silicofluoric in, 134.
as a bactericide, 134.
corrosive action of, on the materials for storing, 134, 135.
Hydrofluosilicic Acid, 135.
specific gravity table, 136.
use of, in the separation of lime and baryta, 136.
Hydrogen Peroxide, 136.
tests for, in ether, 101.
crystallisable, 138.
Hydrogen Sulphide Water, 329, 353, 359.
Hydroxylamine Hydrochloride, 140.
as a reducing agent, 140.

Iceland Spar, 64.
Indicators and Test Papers, 140, 334.
tables of sensitiveness of, 141, 143.
Indigo, 146.
solution, standard, 146, 148.
valuation of commercial, 146.
varieties of, 147.
Indigo Carmine, 148.
standard solution of, for tannin estimation, 149.
varieties of, 149.
Indigotin, 146.
preparation of indigo solution from, 146.
Iodeosin (Erythrosin), 155.
Iodic Acid, 156.
as a test for morphine, 156.
Iodic Anhydride, 156.
Iodine, 150.
decinormal solution of, 152.
separation of chlorine, bromine, and, 152.
various uses of, 152.
puriss, for iodometry, 153.
Iodine in Zinc Chloride Solution, 154.

Iodine Trichloride, 154.
Iodoform Test for Alcohol, 102.
Iridium Tetrachloride, 156.
Iron, 157.
wire (flower wire), 157.
powder, reduced by hydrogen, 157.
powder, ordinary, 158.
prototartrate solution for oxygen absorption, 353.
titration of ferrous, 161, 163, 270.
Iron Ammonium Sulphate, 161.
preparation of, in powder form, 162.
Iron Chloride (Ferric), 158.
arsenic in, 159.
Iron Chloride (Ferrous), 160.
Iron Sulphate, 162.
Iron Sulphide, 162.
arsenic in, 164.

Keiffer's Reagent, 94.
Knapp's Standard Mercuric Cyanide, 165, 191.

Lacmoid (and Diazoresorcin), 165.
Lacmoid Paper, 167.
Lactic Acid, 167.
as a solvent for albuminoids, 167.
Lead, 168.
free from silver, 168.
other varieties of, 168.
Lead Acetate, 168.
Lead Acetate (Basic), 169.
Lead Carbonate (Basic), 170.
Lead Chromate, 170.
estimation of chromic acid in, 171.
presence of carbonic acid in, 172.
commercial varieties, 172.
adulterations of, 172, 173.
Lead Oxide, 173.
litharge, 174.
red lead, 174.
Lead Paper, 169.
Lead Peroxide, 175.
manganese in, 175.
Lead Subacetate, 169, 176.
Lime Water, preparation of, 354.
Litharge, 174.
Lithium Carmine, 73.
Litmus, 176.
tincture, 177.
paper, blue, red, and neutral, 178.
Logwood Tincture, 179.
Luteol, 179.

Magnesia Mixture, 182.
Magnesium, 179.
amalgam, 180.
presence of arsenic in, 180.
Magnesium Carbonate, 180.
heavy, 181.
Magnesium Chloride, 181.
Magnesium Oxide (Calcined Magnesia), 182.
free from sulphuric acid, 183.
Magnesium Sulphate, 184.
Manganese Dioxide, 185.
valuation of, 185.
use of, in the manufacture of bleaching powder, etc., 185.
Manganese Metaphosphate, 186, 227.
Manganese Sulphate, 186.
use of, in the estimation of oxygen, 187.
Manganous Chloride, 184.
use of, in the estimation of oxygen, 185.
Mayer's Solution, 191, 355.
Mercuric Nitrate, 190.
Mercuric Nitrate Solution, standard, 190.
Mercuric Nitroso-nitrate Solution (Millon's reagent, etc.), 190.
Mercuric Oxide, 191.
modifications of, 192.
Mercurous Nitrate, 192.
Mercury, 188.
Mercury, Bichloride, 188.
Meta-diamido-benzene, 192.
Meta-phenylene-diamine, 192.
Meta-phenylene-diamine hydrochloride, 193.
as a test for nitrites, etc., 193.
preparation of the reagent, 193.
Meta-phosphoric Acid, 227.
Methyl Alcohol, 16.
Methyl Orange, 194.
comparative tests with, as indicator, 195.
Methyl Para-phenylene-diamine (di and tetra), 194.
Methyl Violet, 196.
Methylene Blue, 194.
aqueous, preparation of, 353.
Microcosmic Salt, 285.
Millon's Reagent, 190, 219.
Molisch's Sugar Test, 199, 336.
Molybdenum Solution for phosphoric acid estimation, 197, 198.
Molybdic Acid, 196.
free from ammonia, 199.
as a test for alcohol, 198.

α-**Naphthol,** 199.
α-**Naphthol-Potash Test,** for chloroform, etc., 199.

β-Naphthol, 200.
β-Naphthol-benzylamine, 200.
β-Naphtho-Quinone-a-oxime, 200.
α-Naphthylamine Hydrochloride, 201.
Naphthol Carbonimide, 200.
Nessler's Reagent, 189, 201.
Nitric Acid, 201.
test for sulphuric acid in, 202.
normal solution of, 203.
specific gravity tables, 204-209.
fuming, 209.
crude, 210.
table for the correction of the sp. gr. of containing hyponitric acid, 211.
estimation of hyponitric in, 210.
o-Nitrobenzaldehyde, 212.
Nitron, 212.
Nitrophenol, 212.
Nitrophenyl-propiolic Acid, 212.
Nitroso-β-Naphthol, 213.
use of, in quantitative analysis, 213.
Normal Alkalies and Acids, 257.
normal caustic potash, 257.
,, caustic soda, 257, 305.
,, hydrochloric acid, 129, 257.
,, nitric acid, 203, 257.
,, oxalic acid, 215, 257.
,, sulphuric acid, 257, 326.
,, (deci) iodine, 152.
,, (deci) potassium permanganate, 270.
,, (deci) silver nitrate, 284.
,, (deci) sodium chloride, 302.
Nylander and Almen's Reagent, 57.

Oil of Cloves, 108, 213.
Oleum, 328.
Osmic Acid, 213.
Oxalic Acid, 213.
anhydrous, 215.
normal solution of, 215.
Ozone Paper, 118, 334, 349.

Palladium, estimation of, in alkaline palladious chlorides, 216.
Palladium and its Salts, 215.
Palladium Asbestos, 216.
Palladium Black (spongy palladium), 215.
Palladium en chaux, 216.
Palladium, Nitrate, 217.
Palladium Monoiodide, 152, 216.
Palladium Protochloride, 152, 217.
Palladium Wire, 216.
Paranitrophenol, 217.
Perchloric Acid, 217.
preparation of, 218.
Petroleum Ether, 106.
Pfugge's Reagent, 191.
Phenacetolin, 218.
preparation of, 218.
Phenol (carbolic acid), 219.
Phenol Phthalein, 219.
preparation of, 220.
Phenol-Sulphonic Acid, preparation of, 219, 221
Phenyl Hydrazine, 221.
various uses of, 221.
Phloroglucin, 221.
presence of diresorcin in, 221.
colour reactions of, 222.
Phloroglucin and Vanillin Reagent, 223.
Phospho-antimonic Acid, preparation of, 354.
Phospho-molybdic Acid, 223.
as a reagent for alkaloids, 223.
preparation of, 355.
Phospho-tungstic Acid, 224.
as a reagent for alkaloids, 224.
preparation of, 355.
Phosphoric Acid, 224.
brucine test for nitric acid in, 224.
specific gravity table, 226.
Phosphoric Acid, Meta, 226.
as a test for albumen, 227.
analyses of various samples, 227.
Phosphoric Anhydride, 227.
as a drying agent, 227.
presence of lower oxides in, 227.
Phosphorite, 69.
Picric Acid, 229.
test for mono- and dinitro-phenol in, 229.
its liability to explode, 230.
aniline oil, 353.
Picrocarminate of Ammonia, 73, 230.
Picrocarmine, 73, 230.
Picrolonic Acid, 230.
Platinum, 230.
black, 230, 231.
spongy, preparation of, 230.
presence of iridium in, 230.
preparation of very pure, 231.
Platinum Bichloride, 232.
preparation of $PtCl_4$ from, 232.
use of, in the estimation of potash, 233.
Platinum Bichloride Solution, preparation of, 355.
Poirier's Blue, 233.

Potash Solution, Caustic, 260.
specific gravity tables, 261.
Potassio-Iodide of bismuth, 264, 355.
of cadmium, 264, 355.
of mercury, 264, 355.
of zinc, 264, 355.
Potassium and Sodium Tartrate (Rochelle salts), 109, 273, 353.
Potassium Acetate, 233.
Potassium Bicarbonate 234.
use of, in the preparation of $\frac{n}{10}$ potassium arsenite, 234.
Potassium Bichromate, 234.
estimation of sulphuric acid in, 235.
various uses of, 235.
Potassium Biniodate, 236.
Potassium Bisulphate, 237.
Potassium Bitartrate (cream of tartar), 238.
for standardising purposes, 238.
Potassium Bromate, 239.
as an oxidising agent, 239.
Potassium Bromide, 240.
(and bromate), use of, in the estimation of carbolic acid, 241.
moisture and chlorides in, 241.
Potassium Carbonate, 241.
caustic alkali in, 242.
analyses of various commercial samples, 243.
Potassium Chlorate, 244.
estimation of chloric acid in, 244.
accidents in handling, 245.
presence of lead in, 245.
Potassium Chloride, 245.
for agricultural purposes, 246.
Potassium Chromate, 246.
as an indicator, 247.
use of, in the estimation of quinine, 247.
Potassium Cyanide, 247.
precautions in handling, 248.
for technical purposes, 248.
Potassium Ferricyanide, 248.
estimation of, by hydrogen peroxide, 249.
various uses of, 250.
Potassium Ferricyanide Paper, 131, 251.
Potassium Ferrocyanide, 251.
determination of sulphuric acid in, 251.
use of, in the estimation of strcyhnine, 252.
estimation of, by permanganate, 252.
Potassium Hydrate, 253.
puris, 253.
test for nitric acid in, 254, 255, 258.
Potassium Hydrate (*cont.*).
normal solution of, 257.
pure by alcohol, 258.
ordinary pure, 259.
analyses of, 259.
Potassium Iodate, 260.
as a standard in iodometry, 262.
and starch paper, as a test for sulphuric acid, 262.
Potassium Iodide, 262.
presence of iodate in, 262.
Potassium Iodide Solutions, method of preserving, 264.
Potassium Manganate, 265.
Potassium Nitrate, 265.
presence of perchlorate in, 265.
valuation of, 265.
Potassium Nitrite, 266.
method of removing carbonate from, 267.
Potassium Oxalate, neutral, 268.
as a test for quinine, 268.
Potassium Perchlorate, 268.
preparation of, 269.
Potassium Periodate, 269.
Potassium Permanganate, 269.
decinormal solution of, 270.
free from sulphuric acid, 271.
Potassium Persulphate, 272.
Potassium Pyroantimoniate (acid), 272.
Potassium Sodium Tartrate, 273.
Potassium Sulphate, 273.
Potassium Sulphide, 274.
preparation of, 274.
solution (mono), preparation of, 274.
Potassium Sulphocyanide, 275.
paper, 275.
Potassium Sulphydrate, 274.
solution, 274.
Potassium Tetroxalate, 276.
as a standard in volumetric analysis, 276.
Pyoktanin, 196.
Pyridine, 277.
Pyrogallic Acid, 277.
alkaline solution of, for gas analysis, 277.
colour reactions of 278.
Pyrogallol Dimethyl Ether, 278.
Pyrolusite, 196.
Pyrrol, 278.
as a test for lignin, 278.

Reagent Solutions, preparation of, according to Blochmann, 356.
Reagents, preparation of the ordinary, 351.

Red Lead, 174.
Resazurin, 166.
Resorcin, 279.
reactions of, with various compounds, 280.
Resorcin Reagent for nitrous acid, 280.
Rochelle Salts (potassium and sodium tartrate), 109, 353.
Rosolic Acid, 281.
Rubine S. (see Acid fuchsine), 113.
Ruthenium Red, 281.

Saccharose, 321.
preparation of pure, 110.
Sachsse's Standard Mercuric Iodide, 191, 281.
Salicylic Acid, 281.
as a preservative, 282.
Salicyl-sulphonic Acid, preparation of, 282.
Scarlet (see Fuchsine), 112
Schiff's Reagent for aldehydes, 282.
Schiff's Reagent (ammonium thioacetate), 318.
Selenite, 69.
Silver, 282.
lace, for reducing purposes, 283.
preparation of absolutely pure, 283.
grain, precipitated by copper, 283.
Silver Nitrate, 283.
determination of impurities in, 283.
decinormal solution of, 284.
ammoniacal solution of, as a test for aldehydes, 284.
Silver Nitrite, 284.
test of, by Lunge's method, 267.
preparation of, 285.
Soda Lime, 285.
Soda Solution, Caustic, 308.
specific gravity table, 309.
Sodio - ammonium Phosphate (microcosmic salt), 285.
use of, in standardising uranium solutions, 286, 298.
Sodio-Cobaltic Nitrite, 85.
solution, preparation of, 310.
Sodio-Gold Chloride, 106.
Sodium, 286.
amalgam, 286.
safe methods of preserving, 286.
Sodium Acetate, 287.
as a test for alkaloids, 288.
Sodium Bicarbonate, 288.
for the preparation of anhydrous carbonate, 281, 291.
Sodium Bicarbonate (*cont.*).
investigations of the German Pharmaceutical Society on, 289.
estimation of monocarbonate in, 289.
estimation of ammonia in, 291.
Sodium Bichromate, 292.
analyses of commercial, 292.
Sodium Bisulphate, 292.
Sodium Bisulphite, 293.
as a strong reducing agent, 294.
Sodium Borate (Borax), 294.
refined borax, calcined borax and borax glass, 296.
as a standard for acid solutions, 296.
Sodium Bromate, 296.
Sodium Carbonate (pure crystallised), 296.
preparation of absolutely pure, 298.
Sodium Carbonate (pure anhydrous), 298.
anhydrous, test for alkaline hydrate in, 299.
anhydrous, as a standard in acidimetry, 299.
anhydrous, commercial varieties of, 299.
crude (soda ash), 300.
Sodium Chloride, 301.
decinormal solution of, 302.
ordinary (common salt), 302.
ordinary, analyses of various samples, 303.
Sodium Fluoride, 303.
estimation of sulphuric acid and chlorine in, 303.
composition of commercial, 304.
Sodium Hydrate, 304.
pure from sodium, 305.
normal solution of, 257, 305.
pure by alcohol, 305.
presence of boracic acid in, 306.
ordinary pure, 307, 308.
estimation of, in presence of carbonate, 307.
ordinary commercial, 308.
Sodium Hydrosulphide Solution, 316.
Sodium Hypobromite Solution, for the estimation of nitrogen, 57.
Sodium Nitrate, 310.
analyses of commercial, 311.
Sodium Nitrite, 312.
average composition of commercial, 312.
Sodium Nitroprusside, 313.
various uses of, 313.

Sodium Peroxide, 139, 313.
estimation of mercury salts by, 189.
Sodium Phosphate, 313.
Sodium Pyrophosphate, 315.
use of, in electrolysis, 315.
Sodium Succinate, 315.
Sodium Sulphate, 316.
Sodium Sulphide, 316.
preparation of standard solution of, 317.
Sodium Sulphite, 317.
Sodium Thioantimoniate, 317.
Sodium Thiosulphate, 317.
decinormal solution of, 318.
100 per cent., 319.
Sodium Tungstate, 319.
Starch, 320.
soluble, 321.
Sugar, 320.
grape, 109, 320.
cane, 321.
Sulphanilic Acid, 321.
use of, in nitrous acid test, 321.
6 = Sulpho-β = Naphtholazo = m = Oxybenzoic Acid, 321.
Sulphocyanides, test for chlorine in presence of, 39.
Sulphuretted Hydrogen, or Hydrogen sulphide water, 329.
titration of, by iodine, 164.
Sulphuric Acid, 322.
test for arsenic in, 323.
specific gravity table, 324, 325.
specific gravity table of highly concentrated, 326.
normal solution of, 257, 326.
free from nitrogen, 326.
commercial, 327.
fuming, 328.
Sulphuric Anhydride, 328.
Sulphurous Acid, 329.
anhydrous (100 per cent.), 329.
gas, preparation of, 329.

Tannic Acid, separation of, from gallic acid, 330.
methods for the estimation of, 331.
valuation of, as a mordant, 331.
Tannin (tannic acid), 330.
Tartaric Acid, 332.
presence of lead in, 333.
Test Papers, 334.
precautions in testing sensitiveness of, 331.
Tetraiodo-fluorescein, 155.
Tetra = Methyl Para = Phenylene-Diamine, 194.
Thallium Carbonate, 334.
Thallium Paper (Ozone Paper), 334.
Thallous Nitrate, 334.
Thioacetic Acid, 335.
ammonium salt of, 335.
Thiobarbituric Acid, 335.
Thiosinamine, 336.
Thoulet's Solution, 191.
Thymol, 336.
Tin, 336.
powder, pure, preparation of, 337.
commercial varieties of, 337.
Tin Perchloride Solution, 338.
Tin Protochloride, 337.
Tin Protochloride Solution, 128, 338.
Titanic Acid, 338.
Titanium Trichloride, 339.
Titanous Chloride, 339.
Tropæolin oo, 339.
Tropæolin ooo, 339.
Tungstic Acid, 320.
Turmeric, preparation of the tincture, 339.
Turmeric Paper, 339.

Uranium Acetate, 340.
Uranium Nitrate, 341.

Waller's Solution, 154.
Water, Distilled, 341.
preparation of, 342.
presence of ammonia in, 342.
Weselsky's Indicator, 166.
Whiting, 64.
Wijs' Solution, 154.

Xylidine, 343.

Zinc, 343.
note on the determination of iron in, 344.
note on the arsenic test, 345.
quantity of impurities present in various samples of, 345.
preparation of pure, 346.
absolutely free from arsenic, 346.
Zinc Acetate, 347.
Zinc Chloride, 347.
Zinc Chloride Solution, as a solvent for cellulose, 348.
Zinc Dust, 346.
estimation of sulphur in, 347.
Zinc Iodide, 348.
and starch solution, 349.
Zinc Sulphate, 349.
preparation of, free from iron, 349.

INDUSTRIAL ALCOHOL

A PRACTICAL MANUAL ON THE PRODUCTION AND USE OF ALCOHOL FOR INDUSTRIAL PURPOSES AND FOR USE AS A HEATING AGENT AS AN ILLUMINANT AND AS A SOURCE OF MOTIVE POWER

By JOHN GEDDES McINTOSH

Demy 8vo ($8\frac{3}{4}$ in. × $5\frac{3}{4}$ in.). 250 Pages. With 75 Illustrations in the Text, many full page, including Several Plans and 25 Tables

CONTENTS

Chapter I.—Alcohol and its Properties—Ethylic Alcohol — Absolute Alcohol — Adulterations — Properties of Alcohol — Fractional Distillation — Destructive Distillation — Products of Combustion — Alcoholometry — Proof Spirit — Analysis of Alcohol—Table showing Correspondence between the Specific Gravity and Per Cents. of Alcohol over and under Proof—Other Alcohol Tables.

Chapter II.—Continuous Aseptic and Antiseptic Fermentation and Sterilisation in Industrial Alcohol Manufacture.

Chapter III.—The Manufacture of Industrial Alcohol from Beets—Beet-slicing Machines — Extraction of Beet Juice by Maceration, by Diffusion—Fermentation in Beet Distilleries—Plans of Modern Beet Distillery.

Chapter IV.—The Manufacture of Industrial Alcohol from Grain — Plan of Modern Grain Distillery.

Chapter V. — The Manufacture of Industrial Alcohol from Potatoes — The Marienfelde Potato Distillery, Berlin.

Chapter VI.—The Manufacture of Industrial Alcohol from Surplus Stocks of Wine, Spoilt Wine, Wine Marcs, and from Fruit in General—Plans.

Chapter VII. — The Manufacture of Alcohol from the Sugar Cane and Sugar-Cane Molasses—Plans.

Chapter VIII.—Plant, etc., for the Distillation and Rectification of Industrial Alcohol—The Caffey and other "Patent" Stills — Intermittent versus Continuous Rectification — Continuous Distillation — Rectification of Spent Wash—Guillaume's System—Barbet's System.

Chapter IX. — The Manufacture and Uses of Various Alcohol Derivatives, Ether, Haloid, Ethers, Compound Ethers, Chloroform — Methyl and Amyl Alcohols and their Ethereal Salts, Acetone — Barbet's Ether, Methyl Alcohol and Acetone Rectifying Stills.

Chapter X.—The Uses of Alcohol in Manufactures, etc.—List of Industries in which Alcohol is used, with Key to function of Alcohol in each industry.

Chapter XI.—The Uses of Alcohol for Lighting, Heating, and Motive Power.

Index.

Price 8s. 6d. net (Post Free, 9s. Home and Abroad)

Published by

SCOTT, GREENWOOD & SON

8 BROADWAY, LUDGATE, LONDON, E.C. 4

CHEMICAL WORKS

THEIR DESIGN, ERECTION, AND EQUIPMENT

By S. S. DYSON and S. S. CLARKSON

Royal 8vo ($9\frac{3}{4}$ in. × $6\frac{1}{2}$ in.) 220 Pages
80 Illustrations and 9 Folding Plates

CONTENTS

CHAPTER

I. Choice of Site.

II. Notes on Materials used in Construction.

III. First Principles in Laying out a Works—Arrangement of Buildings—Stores—Workshops—The Drainage System—Foundations—Retaining Walls—Fire Prevention—Ambulance Arrangements.

IV. The Power House—Boilers—Coal Store—Automatic Weighing Machines—Chimney—Economisers—Steam Engines—Steam Turbines.

V. Sulphuric Acid Plant — General Design — Chambers — Glover Tower—Gay-Lussac Tower—Notes on Vitriol Manufacture—Recent Developments in Vitriol Plant Design and Working.

VI. Hydrochloric Acid Plant.

VII. Nitric Acid Plant.

VIII. Notes on High Explosives Plant.

IX. Sulphate of Ammonia Plant.

X. Notes on Artificial Manure Plant.

XI. General Plant.

PLATES: I. Boiler House, Economiser, and Chimney. II. Sections through Boiler House. III. Sulphuric Acid Chambers, with Chamber Details. IV. Pyrites Burners. V. Glover Tower. VI. Salt Cake Furnace and Pot. VII. Nitric Acid Plant. VIII. Nitric Acid Pot Setting. IX. Superphosphate Dens.

Price 23s. net (Post Free, 23s. 6d. Home; 23s. 9d. Abroad)

Published by

SCOTT, GREENWOOD & SON

8 BROADWAY, LUDGATE, LONDON, E.C. 4

THE UTILIZATION OF WASTE PRODUCTS

A TREATISE ON RATIONAL UTILIZATION, RECOVERY, AND TREATMENT OF WASTE PRODUCTS OF ALL KINDS

BY THEODOR KOLLER

TRANSLATED FROM THE GERMAN

THIRD ENGLISH REVISED EDITION

DEMY 8VO ($8\frac{3}{4}$ IN. × $5\frac{3}{4}$ IN.) 22 ILLUSTRATIONS 345 PAGES

CONTENTS

Introduction.
Chapter I.—The Waste of Towns.
Chapter II.—Blood and Slaughter-house Refuse.
Chapter III.—Fat from Waste.
Chapter IV.—Tannery Waste.
Chapter V.—Leather Waste.
Chapter VI.—Fur and Feather Waste.
Chapter VII.—Waste Horn.
Chapter VIII.—Fish Waste.
Chapter IX.—Mother-of-Pearl Waste.
Chapter X.—Vegetable Ivory Waste.
Chapter XI.—Waste Wood.
Chapter XII.—Cork Waste.
Chapter XIII.—Waste Paper and Bookbinders' Waste.
Chapter XIV.—The By-products of Paper and Paper Pulp Works.
Chapter XV.—The Waste Produced in the Manufacture of Parchment Paper.
Chapter XVI.—Wool Waste.
Chapter XVII.—Silk Waste.
Chapter XVIII.—The Waste Waters of Cloth Factories.
Chapter XIX.—Cotton Spinners' Waste.
Chapter XX.—Jute Waste.
Chapter XXI.—Utilization of Rags.
Chapter XXII.—Colouring Matters from Waste.
Chapter XXIII.—Residues in the Manufacture of Aniline Dyes.
Chapter XXIV.—Dyers' Waste Waters.
Chapter XXV.—Waste Produced in Butter-making.
Chapter XXVI.—Molasses.
Chapter XXVII.—The Waste Liquids from Sugar-works.
Chapter XXVIII.—Fruit.
Chapter XXIX.—Waste Products of the Manufacture of Starch.
Chapter XXX.—Brewers' Waste.
Chapter XXXI.—Wine Residues.
Chapter XXXII.—Indiarubber and Caoutchouc Waste.
Chapter XXXIII.—Amber Waste.
Chapter XXXIV.—Utilization of Turf or Peat.
Chapter XXXV.—Manufactured Fuels.
Chapter XXXVI.—Illuminating Gas from Waste and the By-products of the Manufacture of Coal Gas.
Chapter XXXVII.—By-products in the Treatment of Coal-Tar Oils.
Chapter XXXVIII.—Ammonia Recovery.
Chapter XXXIX.—Petroleum Residues.
Chapter XL.—By-products in the Manufacture of Rosin Oil.
Chapter XLI.—Soap-makers' Waste.
Chapter XLII.—Alkali Waste and the Recovery of Soda.
Chapter XLIII.—Recovery of Potash Salts.
Chapter XLIV.—Sulphur.
Chapter XLV.—Salt Waste.
Chapter XLVI.—Gold and Silver Waste.
Chapter XLVII.—Platinum Residues.
Chapter XLVIII.—Iridium from Goldsmiths' Sweepings.
Chapter XLIX.—Metal Waste.
Chapter L.—Tinplate Waste.
Chapter LI.—Calamine Slimes.
Chapter LII.—Waste Iron.
Chapter LIII.—By-products of the Manufacture of Mineral Waters.
Chapter LIV.—Infusorial Earth.
Chapter LV.—Meerschaum.
Chapter LVI.—Mica Waste.
Chapter LVII.—Slate Waste.
Chapter LVIII.—Broken Porcelain, Earthenware and Glass.
Chapter LIX.—Utilization of Waste Glass.

PRICE 12S. 6D. NET (POST FREE, 13S. HOME; 13S. 3D. ABROAD)

Published by

SCOTT, GREENWOOD & SON

8 BROADWAY, LUDGATE, LONDON, E.C. 4

GETTY RESEARCH INSTITUTE
3 3125 01147 4919